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K₅Mn₃O₆ and Rb₈Mn₅O₁₀, New Charge Ordered *Quasi* One-Dimensional Oxomanganates (II, III)

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Dedicated to Professor Hans-Jörg Deiseroth on the Occasion of His 70th Birthday

Keywords: Azide/nitrate route; Chain structures; Mixed-valent compounds; Magnetic properties; Density functional calculations

Abstract. K₅Mn₃O₆ and Rb₈Mn₅O₁₀ have been synthesized via the azide/nitrate route from stoichiometric mixtures of MnO and KNO₃/KN₃, or RbNO₃/RbN₃, respectively. The two new members of manganese (II/III) mixed-valent oxides have been studied by single-crystal X-ray diffraction, magnetic susceptibility measurements and density functional theory calculations (DFT). Both crystal structures [K₅Mn₃O₆: *Pna2*₁, *Z* = 4, *a* = 1632.43(7), *b* = 970.07(4), *c* = 616.48(3) pm, *R*₁ = 0.051; Rb₈Mn₅O₁₀: *P2*₁/*c*, *Z* = 8, *a* = 1223(2), *b* = 2717(3), *c* = 1220(2) pm, β = 118.25(2)°, *R*₁ = 0.086] display quasi one-dimensional [MnO₂]^{*n*-} chains, composed of edge sharing MnO₄ tetrahedra.

Introduction

Multinary oxides display an overwhelming diverseness in compositions and structures, resulting in quite relevant physical properties. Thus, it is well understandable that this class of matter continues to be in the focus of current efforts in sciences and engineering. Particular attention is being paid to materials exhibiting the bulk properties of magnetoresistance (GMR) and superconductivity (HTSC). Although known for decades, the macroscopic phenomena of GMR and HTSC in oxides are still not fully understood on the microscopic level. There seems to be consensus about the crucial factors of influence, as there are electron correlation in combination with charge, spin and orbital ordering on special lattices.^[1] However, these ingredients are heavily entangled resulting in a virtually indigestible complexity. The situation is aggravated by the fact that the periodicities of most of the GMR and HTSC materials are significantly perturbed, impairing rigorous theoretical treatment and smearing experimental response.^[2]

One option to unravel this confusing pattern of interactions would be to reduce the complexity by fixing part of the degrees of freedom. In following this notion, we have started investigating oxide systems that show charge, spin and orbital

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Complete charge ordering of Mn^{2+} and Mn^{3+} is observed along the chain direction with repetition units $[-Mn^{3+}-Mn^{2+}-Mn^{2+}-]$ resulting for $K_5Mn_3O_6$, and $[-Mn^{3+}-Mn^{2+}-Mn^{2+}-Mn^{3+}-Mn^{2+}-]$ for $Rb_8Mn_5O_{10}$. Magnetic susceptibility data as well as DFT calculations indicate strong *anti*-ferromagnetic intra-chain coupling to be present already at ambient temperature, and above. $Rb_8Mn_5O_{10}$ features three-dimensional spin ordering below $T_N = 10.9$ K, mediated by ferromagnetic coupling between the chains, while such a 3D coupling appears to be frustrated in $K_5Mn_3O_6$.

ordering, however, on a fully periodic lattice. Among them are intrinsically doped sodium cuprates,^[3-11] featuring strands of trans-edge sharing CuO₄ squares. These virtually one dimensional partial structures are providing a wealth of particular ordering phenomena, among others they represent unambiguous manifestations of Wigner lattices,^[5] are magnetically frustrated,^[7-9] or undergo magnetic excitations across the Wigner gap.^[11] As a similarly prolific new class of compounds, alkali manganates (II/III) of general composition $A_r MnO_2$ (A = K, Rb, Cs)^[12–16] have become available through the Azide/Nitrate route of synthesis.^[17,18] Interestingly, this new series of oxomanganates adds to the few examples of ternary manganese II/III mixed valent compounds, like so far reported Na₂₆Mn₃₉O₅₅^[19] or LiMn₃O₄.^[20] This is constituting quite a contrast to the vast number of manganese (III/IV) mixed oxides known. In addition, the synthetic procedure applied allows to precisely and reproducibly fix the Mn²⁺/Mn³⁺ ratio, and to scale up to gram amounts.

Part of these new alkali manganates show commensurably modulated structures, e.g. $Cs_3Mn_2O_4$,^[15] others display small periodicities, like $Rb_{15}Mn_{11}O_{22}$.^[14] They all share the same basic architecture, in forming doped quasi one dimensional polyanionic chains $[MnO_2]^{n-}$ of trans-edge sharing tetrahedra, which are centering hexagonal channels, arranged following a honey comb pattern. The walls of the channels are decorated with the alkali ions. As a result, the electronic and magnetic interactions are highly anisotropic, and virtually one dimensional along the MnO_2 chain directions.

Here we report on new members of this family, $K_5Mn_3O_6$ and $Rb_8Mn_5O_{10}$, their crystal structures and magnetic proper-

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ties determinations. Electronic and magnetic structural features are further analyzed by density functional theoretical (DFT) calculations.

Results and Discussion

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The title compounds K5Mn3O6 and Rb8Mn5O10 have been synthesized along the azide/nitrate route[17,18] as pure phases. The black compounds are very sensitive to air and moisture. Their crystal structures were determined from single-crystal Xray diffraction data collected at 298 K. The details for data collection, structural parameters, and atomic coordinates are given in Table 1, Table 2, and Table 3. As shown in Figure 1 and Figure 2, both crystal structures are characterized by the presence of one-dimensional [MnO₂]ⁿ⁻ polyanions constituted

Table 1. Crystal data and structure refinement data of K₅Mn₃O₆ and Rb₈Mn₅O₁₀, at 298 K.

	K ₅ Mn ₃ O ₆	$Rb_8Mn_5O_{10}$		
Formula weight	456.32	1118.46		
Space group (no.), Z	<i>Pna</i> 2 ₁ (33), 4	$P2_1/c$ (14), 8		
Lattice constants /pm, °	a = 1632.43(7)	a = 1223(2)		
	b = 979.07(4)	b = 2717(3)		
	c = 616.48(3)	c = 1220(2)		
		$\beta = 118.25(2)$		
$V/Å^3$, $\rho_{\rm xray}/g\cdot {\rm cm}^{-3}$	985.30(8), 3.076	3571(8), 4.160		
Crystal size /mm ³	$0.25 \times 0.15 \times 0.10$	$0.25 \times 0.10 \times 0.08$		
Diffractometer	SMART APEX I,	SMART APEX II,		
	Bruker AXS	Bruker AXS		
X-ray radiation, λ /pm	71.073			
Absorption correction	SADABS ^[26]			
2θ range /°	2.49-80.65	1.49-52.00		
Index range	$-29 \le h \le 29$	$-14 \le h \le 15$		
	$-17 \le k \le 17$	$-33 \le k \le 33$		
	$-11 \le l \le 11$	$-14 \le l \le 14$		
Reflection collected	27466	19046		
Data, <i>R</i> _{int}	6160, 0.028	7042, 0.137		
BASF	0.50(4)	0.507(3)		
No. of parameters	128	416		
Transmission: t_{max} , t_{min}	0.501, 0.363	0.238, 0.061		
$R_1[F^2 > 2\sigma(F^2)]$	0.051	0.086		
$wR(F^2)$	0.125	0.274		
$\Delta \rho_{\rm max}$, $\Delta \rho_{\rm min}$ /e·Å ⁻³	2.56, -1.63	2.58, -2.32		
Deposition no.	CSD-428944	CSD-428945		

Table 2. Atomic coordinates and equivalent displacement parameters $U_{\rm eq}$ /pm² for K₅Mn₃O₆ at 298 K.

Atom	Site	х	У	Z	U_{eq}
Mn1	4a	0.08103(4)	0.22600(7)	0.369381)	144(1)
Mn2	4a	-0.08748(4)	0.248699(7)	0.3507(1)	162(1)
Mn3	4a	0.24981(4)	0.22875(8)	0.4335(1)	160(1)
K1	4a	-0.08742(7)	-0.0821(1)	0.3642(2)	248(2)
K2	4a	0.11193(9)	-0.1107(1)	0.3508(3)	330(3)
K3	4a	-0.00266(7)	0.4131(1)	0.7504(2)	207(2)
K4	4a	0.21271(9)	0.5576(2)	0.4548(2)	318(3)
K5	4a	0.18433(8)	0.3851(1)	-0.0134(2)	265(2)
01	4a	0.1695(2)	0.1420(4)	0.2183(6)	165(5)
O2	4a	-0.0037(2)	0.1480(4)	0.5346(6)	184(6)
O3	4a	-0.1823(2)	0.1430(4)	0.2383(7)	211(6)
O4	4a	0.3490(2)	0.1419(5)	0.5760(7)	245(8)
05	4a	0.1480(2)	0.3091(5)	0.5873(6)	233(7)
06	4a	0.0103(3)	0.3009(5)	0.1505(7)	256(7)

of edge-sharing, distorted MnO₄ tetrahedra. The alkali metal ions fill the space in between, forming a tubular honeycomblike arrangement. These basic structural principles correspond $K_{29}Mn_{17}O_{34}$,^[12] those previously found for to $Rb_{11}Mn_8O_{16}$, [12,14,16] $Rb_{15}Mn_{11}O_{22}$, [13,14] $Cs_4Mn_3O_6$, [12] and $Cs_3Mn_2O_4$.^[15,16]

Both compounds develop full charge order into di- and trivalent manganese. The oxidation states 2+ and 3+ can be clearly assigned based on the Mn-O bond lengths. The average distances are 204 pm for Mn²⁺-O and 190 pm for $Mn^{3+}-O$. The repetition units are $[-Mn^{3+}-Mn^{2+}-Mn^{2+}-]$ for $K_5Mn_3O_6$ and $[-Mn^{3+}-Mn^{2+}-Mn^{3+}-Mn^{2+}-]$ for Rb₈Mn₅O₁₀. The charge ordering patterns are the same as observed for analogous Na₅Cu₃O₆^[11] and Na₈Cu₅O₁₀,^[4] how-

Table 3. Atomic coordinates and equivalent displacement parameters $U_{\rm eq}$ /pm² for Rb₈Mn₅O₁₀ at 298 K.

Atom	Site	х	у	Z	U _{eq}
Rb1	4e	0.3777(6)	0.0930(2)	0.2211(6)	246(15)
Rb2	4e	0.2295(6)	0.0969(2)	-0.1123(6)	258(16)
Rb3	4e	0.7712(5)	0.2191(2)	0.6035(5)	231(13)
Rb4	4e	0.5886(5)	0.2139(2)	0.2681(6)	250(13)
Rb5	4e	0.1546(6)	0.1516(2)	0.3240(7)	365(17)
Rb6	4e	0.3414(6)	0.1632(2)	-0.3261(6)	274(15)
Rb7	4e	0.1139(5)	0.2180(2)	-0.2305(6)	318(15)
Rb8	4e	0.8090(5)	0.3467(2)	0.6657(6)	228(13)
Rb9	4e	-0.1053(6)	0.0963(2)	-0.2816(6)	259(15)
Rb10	4e	0.7151(5)	0.0908(2)	0.3785(6)	218(15)
Rb11	4e	0.2509(5)	0.2080(2)	0.1007(5)	225(13)
Rb12	4e	0.6827(6)	0.1555(2)	0.8252(6)	244(14)
Rb13	4e	0.2195(7)	0.0230(2)	0.3658(8)	599(22)
Rb14	4e	0.1205(5)	-0.0254(2)	-0.2061(5)	249(13)
Rb15	4e	0.3052(6)	-0.0321(2)	0.1298(6)	328(16)
Rb16	4e	0.3549(6)	0.0354(2)	-0.3018(7)	355(16)
Mn1	4e	0.4882(7)	0.1506(2)	0.5011(8)	128(18)
Mn2	4e	0.0026(7)	0.1515(2)	0.4903(8)	140(18)
Mn3	4e	0.5040(7)	0.1516(2)	-0.0170(7)	124(17)
Mn4	4e	-0.0167(8)	0.1498(2)	0.0064(8)	173(20)
Mn5	4e	0.9531(7)	0.2491(3)	0.9528(7)	179(14)
Mn6	4e	0.4518(7)	0.24883)	0.4546(7)	168(14)
Mn7	4e	0.0266(7)	0.0498(2)	0.5166(8)	208(20)
Mn8	4e	0.5255(8)	0.0501(2)	0.0203(8)	184(19)
Mn9	4e	0.5192(8)	0.0496(2)	0.5261(8)	208(20)
Mn10	4e	0.0177(8)	0.0490(2)	0.0247(8)	250(21)
01	4e	0.967(3)	0.187(1)	0.863(3)	294(84)
02	4e	0.850(2)	0.1884(8)	0.427(2)	86(59)
03	4e	0.538(2)	0.2052(8)	0.606(3)	104(61)
04	40	0.521(3)	0.0996(7)	-0.108(3)	132(66)
05	40	0.521(3)	-0.0083(9)	0.629(3)	219(73)
06	40	0.375(3)	0.0003(9) 0.0987(8)	0.029(3) 0.484(3)	194(74)
07	40	-0.031(6)	0.0907(0)	0.104(3)	185(66)
08	40	0.001(0) 0.111(2)	0.2054(0) 0.2061(8)	0.525(2)	83(59)
09	40	0.959(3)	0.2001(0) 0.1004(8)	0.323(2) 0.372(3)	143(65)
010	40	-0.059(3)	0.1004(0)	-0.132(3)	292(82)
010	40	-0.035(3)	-0.010(1)	-0.132(3) 0.070(3)	365(93)
012	40	0.055(3)	-0.011(1) 0.190(1)	-0.037(3)	265(77)
012	40	0.304(3) 0.401(2)	0.190(1) 0.1878(8)	-0.037(3)	127(61)
013	40	0.401(2) 0.104(4)	0.1070(0)	0.031(4)	503(114)
014	40	-0.104(4)	0.099(1) 0.1100(0)	0.031(4) 0.124(3)	126(62)
015	4e 1 a	0.340(3) 0.084(3)	0.1109(9) 0.100(1)	0.124(3) 0.627(3)	317(82)
010	4e 4 a	0.064(3)	0.109(1) 0.11201)	0.027(3)	256(00)
017	4e	0.033(3) 0.122(3)	0.11281)	0.377(3)	217(07)
010	4e	0.123(3)	-0.000(1)	0.309(3)	34/(0/) 162(62)
019	40	0.388(2)	0.2002(8)	-0.044(3)	103(02)
170	40	U = U = D(4)	11111111	11114 1(4)	114(115)

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Figure 1. Projection of the crystal structures of $K_5Mn_3O_6$, (view along [1 0 0]) and $Rb_8Mn_5O_{10}$ (view along [0 1 0]), with margins of the unit cells (grey lines).

ever, with copper in a square-planar coordination instead of the distorted tetrahedral of manganese in the respective manganates.

The magnetic susceptibilities $\chi(T)$ of both materials, K₅Mn₃O₆ (Figure 3) and Rb₈Mn₅O₁₀ (Figure 4), appear to be considerably reduced by strong magnetic exchange interactions already at ambient temperature. No Curie-Weiss type behavior is seen, and the susceptibilities χ_{mol} vary in a very small range of 0.0018–0.0026 $emu \times mol^{-1}~(K_5 Mn_3 O_6)$ and 0.0016– 0.0032 emu \times mol⁻¹ (Rb₈Mn₅O₁₀). Such a weak, slightly temperature dependent magnetic response has also been found for other alkali metal manganates like Rb₂Mn₃O₄,^[21] $Cs_3Mn_2O_4$,^[15] $Cs_4Mn_3O_6$,^[12] or $K_{29}Mn_{17}O_{34}$.^[12] It is worth mentioning that the anti-parallel ordering of the Mn spins along the chain direction results in an overall anti-ferromagnetic arrangement for both, K₅Mn₃O₆ and Rb₈Mn₅O₁₀ (see Figure 2), while this is not the case for Cs₃Mn₂O₄, where ferrimagnetic intra-chain ordering is observed.^[15] Rb₈Mn₅O₁₀ shows the typical signature for a 3D anti-ferromagnetic transition at the Néel temperature $T_{\rm N} = 10.9$ K, which is absent in K₅Mn₃O₆. Thus, in the family of quasi one-dimensional

manganates under discussion we see two kinds of 3D magnetic ordering behaviors. Some members develop fully ordered spin structures at low temperatures, while for others 3D ordering appears to be frustrated, although the intra-chain exchange coupling is of a strength comparable to the former class. This observation can be related to differences in the charge ordering patterns. In manganates displaying fully ordered 3D spin structures at low temperature, the manganese ions mediating the inter-chain exchange coupling are bearing the same charge, while in the frustrated systems the shortest coupling paths are between Mn³⁺ and Mn²⁺, see Figure 2.



Figure 3. Magnetic susceptibility of K₅Mn₃O₆ vs. temperature at 1 T.



Dedicated Cluster

Figure 4. Magnetic susceptibility of $Rb_8Mn_5O_{10}$ vs. temperature at 1 T.



Figure 2. Cut-offs of the crystal structures of $K_5Mn_3O_6$, $Rb_8Mn_5O_{10}$, and $Cs_3Mn_2O_4$ in comparison, illustrating the different types of charge and spin ordering along the MnO_2 chain directions.

Electronic and magnetic structural properties of K₅Mn₃O₆ and Rb₈Mn₅O₁₀ have been calculated for their experimentally determined geometries using PBE/PAW level approximated DFT.^[22] The charge densities and magnetic moments were self-consistently calculated until the total energies had converged to 10^{-7} eV/cell; the results are reported in Table 4. Analysis of different charge and magnetic ordering along the [MnO₂]ⁿ⁻ chains evidently confirms the experimental fact that the Mn atoms are charge and spin ordered. The theoretical approaches we used to calculate the charge/spin order is described below in theoretical methods. Both the structures are stabilized in an anti-ferromagnetic ground state - AFM1 (AFM coupling in the chains and FM between the chains, see Figure 2). When the spin ordering is anti-ferromagnetically coupled in and between the chains, for K₅Mn₃O₆ this hypothetical AFM2 state is 3.7 meV/unit cell higher in energy than AFM1, indicating the presence of three-dimensional magnetic ordering that may suffer magnetic frustration. The AFM coupling strength between the $[MnO_2]^{n-}$ chains is almost negligible (1.0 meV/unit cell) in Rb₈Mn₅O₁₀; this is underlining the fact that the bulk of the crystal is one-dimensionally charge ordered, corroborating the experimental findings. The 3D ferromagnetic ordered (FM) state is not at all competitive with respect to AFM states (see Table 4).

Table 4. Calculated total charge $T(\rho)$ and spin $S(\rho)$ densities per Mn site, band gaps (E_g) and total energies (E) for $K_5Mn_3O_6$ and $Rb_8Mn_5O_{10}$ in different magnetic order states. FM: ferromagnetic. AFM1: *anti*-ferromagnetic (AFM) in the chains and FM between the chains. AFM2: AFM in and between the chains.

	Mn ²⁺		Mn ³⁺			
	Τ(ρ)	$S(\rho)$	Τ(ρ)	$S(\rho)$	E_{g} /eV	E /eV
K ₅ Mn ₃ O ₆	-	-	-	-	0	
FM	1.2	4.4	1.4	3.6	0.0	3.41
AFM1	1.2	4.2	1.4	3.3	0.1	0.00
AFM2	1.2	4.2	1.4	3.3	0.1	3.7×10^{-3}
Rb ₈ Mn ₅ O ₁₀						
FM	1.2	4.4	1.4	3.6	0.0	11.04
AFM1	1.2	4.2	1.4	3.3	0.1	0.00
AFM2	1.2	4.2	1.4	3.3	0.1	1.0×10^{-3}

The electronic densities of states have been calculated for different magnetic ordering patterns. Fundamentally, the calculated DOS for $K_5Mn_3O_6$ and $Rb_8Mn_5O_{10}$ in AFM1 and AFM2 settings are very similar. Figure 5 shows the AFM1 DOS for both the structures. It is apparent from the DOS shown that the AFM1 structures are magnetically ordered low band gap semiconductors. The band gaps reported should be taken as qualitative estimates, since DFT underestimates the widths of band gaps.^[23] Inspection of the projected density of states (PDOS) shows that Mn (*d*) states are predominant around the Fermi energy level (E_F) with overlap of O (2*p*) states. The bands located in the energy range between -3 to -6 eV are O (2*p*) states with some mix of Mn (*d*).

The spin polarized charge densities or magnetic moments (μ_B) as calculated using the Bader charge partitioning Scheme are in accordance with the oxidation states of Mn atoms as assigned based on the Mn–O bond lengths. The μ_B per Mn



Figure 5. Ground state AFM1 electronic density of states (DOS) for $K_5Mn_3O_6$ (Z = 4) and $Rb_8Mn_5O_{10}$ (Z = 8). The Fermi energy level is shifted to 0 eV.

site are reported in Table 4. These are comparable to the expected spin-only magnetic moments; the residual differences may be attributed to orbital contributions. We note that there is no noticeable spin moment on O sites. The extracted chemical information by integrating the projected densities of states and partitioning of charge density are giving unequivocal support to the fact that the K5Mn3O6 and Rb8Mn5O10 crystal structures are charge and spin ordered. The respective charge ordering patterns are different for the structures under consideration (including Cs₃Mn₂O₄), and are depending prevailingly on the compositions, which fix the Mn²⁺/Mn³⁺ ratio. Minimization of the long range Coulomb energy appears to be a second relevant factor of influence determining the charge order, since the same patterns develop in quasi one dimensional oxomanganates (II,III) and respective cuprates of analogous compositions, thus indicating that the former might represent Wigner crystals, as has been proven valid earlier for the cuprates (II,III).^[5,11]

Conclusions

Two new members of the family of intrinsically doped manganates (II,III), K₅Mn₃O₆ and Rb₈Mn₅O₁₀, are reported. As a dominant structural feature, both compounds display chain-like poly-oxoanions with the charges 2+ and 3+ on the Mn sites fully ordered, and in both cases with similarly strong antiferromagnetic intra-chain exchange interactions already present at ambient temperature. In contrast, the 3D ordering behavior of the two oxomanganates is substantially different. While Rb₈Mn₅O₁₀ is developing a three dimensional antiferromagnetic spin structure at $T_{\rm N}$ = 10.9 K, the inter-chain coupling appears to be frustrated for K₅Mn₃O₆. Similar patterns have been observed for previously reported quasi one-dimensional mixed valent oxomanganates. Empirically, 3D frustration of magnetic order seems to be related to a special structural condition that forces the coupling between adjacent chains to be mediated between manganese atoms in the different oxidation states II and III. For all members A_{1-x} MnO₂ where the inter-chain neighboring manganese atoms are in the www.zaac.wiley-vch.de

same valence state, either 2+ or 3+, three dimensional antiferromagnetic spin structures result.

Experimental Section

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Synthesis: $K_5Mn_3O_6$ and $Rb_8Mn_5O_{10}$ were prepared via the azide/ nitrate route^[17, 18] from MnO, KNO_3/KN_3 , and MnO, $RbNO_3/RbN_3$, respectively. The azides were synthesized by distilling HN_3 into an aqueous solution of K_2CO_3 , or Rb_2CO_3 , respectively. For a detailed prescription see Ref.[24]. All starting materials were dried at 373 K for 12 h under vacuum (10⁻³ mbar) and mixed in the ratio required according to Equation (1) and Equation (2).

 $8 \text{ KN}_3 + 2 \text{ KNO}_3 + 6 \text{ MnO} \rightarrow 2 \text{ K}_5 \text{Mn}_3 \text{O}_6 + 13 \text{ N}_2 \uparrow$ (1)

$$14 \text{ RbN}_3 + 2 \text{ RbNO}_3 + 10 \text{ MnO} \rightarrow 2 \text{ Rb}_8 \text{Mn}_5 \text{O}_8 + 22 \text{ N}_2 \uparrow$$
(2)

In a first step, the starting mixtures were ground thoroughly in an agate mortar (approx. 1 g batches), pressed to pellets ($\emptyset = 10 \text{ mm}$) under 10^5 N , dried in vacuo (10^{-3} mbar) at 400 K overnight, and placed under argon in closed steel containers, provided with silver inlays.^[18] The specially designed containers are equipped with squeeze seals, which withstand the internal pressure to a certain degree, but also let safely escape the considerable amounts of nitrogen formed during the reaction.^[17,18] In a flow of dried argon, the following temperature schedule was applied: 298 K \rightarrow 533 K (100 K h⁻¹); 533 K \rightarrow 653 K (5 K h⁻¹); 653 K \rightarrow 773 K (20 K h⁻¹) and subsequent annealing for 30 h at 773 K. The reaction products were phase pure as confirmed by X-ray powder diffraction.

Hazards: Rapid heating or running the reaction in a gastight welded container can lead to a dangerous explosion!

The alkali metal manganates are very sensitive to humid air and therefore all further manipulations must be run in an inert atmosphere of purified argon.

Structure Determination: Single crystals, of sufficient quality for Xray diffraction, were mounted in glass capillaries inside a glovebox. The diffraction data were collected at 298 K on a SMART-APEX CCD X-ray diffractometers (Bruker AXS, Karlsruhe, Germany) with graphite-monochromated Mo- K_{α} radiation. The reflection intensities were integrated with the SAINT subprogram in the Bruker Suite software package,^[25] a multi-scan absorption correction was applied using SADABS.^[26] The structures were solved by direct methods and refined by full-matrix least-squares fitting with the SHELXTL software package.^[27] It has turned out that both crystals under investigation were merohedrally twinned. The twin-laws [-1 0 0, 0 -1 0, 0 0 -1] for inversion-twins was used for the K5Mn3O6 crystal, and [0 0 1, 0 -1 0, 1 0 0] for pseudo-merohedral inversion twins had to be applied in the case of Rb₈Mn₅O₁₀ during the refinements, in order to obtain meaningful displacement parameters for the oxygen atoms. Experimental details are given in Table 1, atomic coordinates and displacement parameters are listed in Table 2 and Table 3.

Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fizkarlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository numbers CSD-428944, and CSD-428945.

Magnetic Susceptibility: Magnetic susceptibilities $\chi(T)$ were measured on powder samples of about 30 mg with a Magnetic Properties

Measurements System (MPMS, Quantum Design, San Diego, CA). The susceptibilities were recorded at H = 0.0006, 0.01, 0.1, 1, 3 and 7 T in the temperature range of 2–350 K. The specimens were sealed in quartz tubes under helium, the raw data were corrected for the sample holder contribution and for the diamagnetic contributions of the constituting elements.

Theoretical Methods: Spin-unpolarized and spin-polarized density functional theory calculations were carried out using the Vienna *ab inito* simulation package (VASP),^[22] applying the projector-augmented wave (PAW)^[28,29] method and Perdew-Burke-Ernzerhof exchange correlation functional of generalized gradient approximation (GGA).^[30] The PAW potentials present the valence electrons of K (3s², 3p⁶, 4s¹), Rb (4s², 4p⁶, 5s¹), Mn (3d⁶, 4s¹), and O (2s², 2p⁴). The cut-off energy for the planewaves was set to 400 eV and the Brillouin zone integration was sampled using a 4 × 4 × 4 Monkhorst-Pack *k*-points mesh.^[31] The convergence of the magnetic moments were carefully checked by supplying different initial magnetic configurations. In order to obtain the magnetic moments per site, Bader charge analysis was done on a charge density grid.^[32,33]

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