

Supporting information for the paper

Preparation, crystal chemistry and hidden magnetic order in the family of trigonal layered tellurates

$A_2Mn(4+)TeO_6$  ( $A = Li, Na, Ag, Tl$ )

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### 1. Starting materials

All chemicals were of reagent grade. Carbonates and nitrates of lithium, sodium and potassium were dried at 150 °C; tellurium dioxide (paratellurite) and manganese sesquioxide were calcined at 400 °C; potassium chloride, potassium permanganate, silver nitrate, thallium (I) nitrate, and amorphous tellurium trioxide were used as received. All dried reagents and synthesis products were stored in closed containers in a desiccator.

### 2. Synthesis and characterization of NaMnO<sub>2</sub>

Equimolar amounts of Mn<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> were carefully mixed with a mortar and pestle, pressed and calcined in air for 4 h at 800 °C with intermittent grinding and pressing. In some preparations, 5 % of Na<sub>2</sub>CO<sub>3</sub> was substituted by equivalent amount of NaNO<sub>3</sub> to intensify the reaction. XRD confirmed formation of the low-temperature monoclinic layered  $\alpha$ -modification of NaMnO<sub>2</sub>. However, the powdered compound was found to be unstable in air, as manifested by rapid degradation of its basal reflection with  $d = 5.32 \text{ \AA}$  and simultaneous growth of the basal reflection of the reaction product,  $d = 5.60 \text{ \AA}$  (Fig. S1), whereas reflections with small or zero contribution of the lattice parameter  $c$  (e.g.,  $hk0$ ,  $hk1$ ) did not changed significantly. At least three reaction types or their combinations might be suggested to explain the observed effects:



As prepared and freshly ground NaMnO<sub>2</sub> was brown but rapidly turned black. This supports the oxidation hypothesis that implies a mixed-valence state.

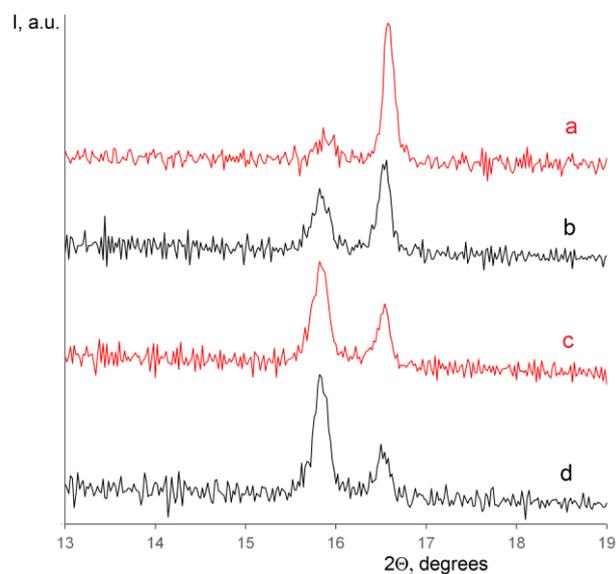


Fig. S1. Basal (0 0 1) reflections from  $\alpha$ - $\text{NaMnO}_2$  and its conversion product measured in ambient air successively four times with scan rate of  $5^\circ/\text{min}$ . Intervals between starting scans a and b, b and c, c and d were 13, 9 and 6 minutes, respectively.

### 3. Synthesis and characterization of $\text{Na}_2\text{MnTeO}_6$

As indicated in the main text, the best samples of  $\text{Na}_2\text{MnTeO}_6$  were prepared from  $\text{NaMnO}_2$ ,  $\text{NaNO}_3$  and  $\text{TeO}_2$ , although “direct” preparation (without  $\text{NaMnO}_2$ ) was also tested. In some instances, 20-30 % of  $\text{NaNO}_3$  was substituted with equivalent amount of  $\text{Na}_2\text{CO}_3$ . The mixture was pressed into thin discs, 25 mm in diameter, and introduced into a preheated furnace at  $600$ - $650^\circ\text{C}$ . After 1-2 hours, it was removed, cooled, reground, pressed and calcined again at  $650$ - $720^\circ\text{C}$ . At  $700$ - $720^\circ\text{C}$ , the pellets were surrounded with packing powder of the same composition to prevent possible loss of volatile components.

Instability of the starting  $\text{NaMnO}_2$  in air was a challenge. Of course, the reactions listed in the preceding Section did not change the gross Na/Mn ratio in the sample, and all the absorbed components were eliminated during subsequent heat treatment to prepare  $\text{Na}_2\text{MnTeO}_6$ . However, there remained a problem of accurate dosage of the manganite powder. In some instances, we used very fast grinding and weighing this “ $\text{NaMnO}_2$ ” with arbitrarily chosen excesses, 0.5-5 %. Otherwise, we did not grind a sintered pellet. Instead, just after its removal from the furnace and cooling for about a minute, it was rapidly broken into few pieces, and they, still hot, were placed in separate small weighed glass containers, closed tightly and put into a desiccator. After complete cooling, a container might be weighed and corresponding amounts of other reagents might be calculated and weighed proportional to the obtained net weight of  $\text{NaMnO}_2$ . Then, the pieces of  $\text{NaMnO}_2$  were ground together with other reagents with no need in protecting atmosphere. However, neither of the two approaches could guarantee strict stoichiometry, as manifested in occasional appearance of foreign phase(s) (Fig. 2 and Table S1), lattice parameter variations (Table S1) and deviations in the analytical data (Table 1).

Insufficient amount of NaMnO<sub>2</sub> resulted in appearance of Na<sub>2</sub>TeO<sub>4</sub> impurity. To convert it into Na<sub>2</sub>MnTeO<sub>6</sub>, small amounts of manganese nitrate was sometimes added. This compensated for Mn deficiency but could not compensate for the corresponding sodium deficiency and might result in sodium-deficient crystals, e.g., Na<sub>2-2x</sub>Mn<sub>1-x</sub>Te<sub>1+x</sub>O<sub>6</sub>.

Table S1. Preparation conditions and XRD data for several nominal Na<sub>2</sub>MnTeO<sub>6</sub> samples

No.	Starting mixture	Heat treatment*	Phases	<i>a</i> , Å	<i>c</i> , Å	<i>c/a</i>
1**	1.02 “NaMnO <sub>2</sub> ” + TeO <sub>2</sub> + 1.05 NaNO <sub>3</sub>	650 °C, 1 h	2H + trace 3R and Na <sub>2</sub> TeO <sub>4</sub>	5.1189(20)	10.5694(3)	2.0648
2	1.005 “NaMnO <sub>2</sub> ” + TeO <sub>2</sub> +0.7 NaNO <sub>3</sub> + 0.15 Na <sub>2</sub> CO <sub>3</sub>	650 °C, 1 h + 670 °C, 3h	2H + more 3R + trace Na <sub>2</sub> TeO <sub>4</sub>	Not measured		
3	“NaMnO <sub>2</sub> ” + TeO <sub>2</sub> + NaNO <sub>3</sub>	650 °C, 1 h	2H + Na <sub>2</sub> TeO <sub>4</sub>	Not measured		
4	Sample 3 + several drops of strong Mn(NO <sub>3</sub> ) <sub>2</sub> solution	400 °C, 15 h + 650 °C, 2 h	2H + trace 3R	5.1162(11)	10.5656(1)	2.0651
5	1.005 “NaMnO <sub>2</sub> ” + TeO <sub>2</sub> + NaNO <sub>3</sub>	650 °C, 1+1 h	3R + 2H + trace Na <sub>2</sub> TeO <sub>4</sub>	5.1249(17)	15.9277(3)	3.1079
				5.117(6)	10.621(17)	2.076
5A**	Sample 5 + several drops of strong Mn(NO <sub>3</sub> ) <sub>2</sub> solution	300 °C, 1 h + 700 °C, 1+3 h	2H only	5.1107(13)	10.557(10)	2.0656
6	1.005 “NaMnO <sub>2</sub> ” + TeO <sub>2</sub> +0.8 NaNO <sub>3</sub> + 0.1 Na <sub>2</sub> CO <sub>3</sub>	650 °C, 1h + 700 °C, 2 h	2H + trace 3R	5.1138(7)	10.5640(1)	2.0658
7	NaMnO <sub>2</sub> + TeO <sub>2</sub> + NaNO <sub>3</sub>	650 °C, 1h + 720 °C, 5 h	2H only	5.1088(8)	10.5485(1)	2.0648
8	0.75 Na <sub>2</sub> CO <sub>3</sub> + 0.5 NaNO <sub>3</sub> + 0.5 Mn <sub>2</sub> O <sub>3</sub> + 1.005TeO <sub>3</sub>	600 °C, 1 h + 650 °C, 3h	3R + 2H + Na <sub>2</sub> TeO <sub>4</sub>	Not measured		
8A	Sample 8	700 °C, 1h	2H + trace 3R and Na <sub>2</sub> TeO <sub>4</sub>	5.1304(18)	10.6147(4)	2.069

\*Plus mark in the column ‘Heat treatment’ stands for quenching, grinding and pressing

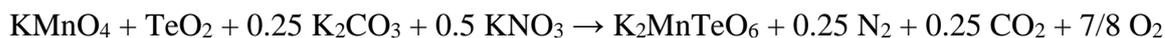
\*\*Internal standard was not used for this sample; thus, lattice parameters are less accurate than their ratio

Another problem that might contribute to the above variations was possible macroscopic inhomogeneity of the starting pellet, if molten NaNO<sub>3</sub> was not completely fixed by capillary forces and might flow to the bottom of the vertical pellet and even out of the pellet. Indeed, in the first preparations, the calcined pellet was strongly deformed and attached to the crucible. Then, to reduce fraction of the liquid phase, a portion of the fresh mixture of reagents was mixed with approximately the same amount of

previous calcination. As a result, the pellets were not deformed or attached to their crucibles. This approach was used in synthesis of the largest sample 6 (about 35 g), targeted to preparation of the four  $A_2MnTeO_6$  samples for future neutron diffraction. Sample 6 was prepared in three successive portions. Before the final calcination, all of them were carefully mixed together to provide uniform composition. Table S1 summarizes results of several  $Na_2MnTeO_6$  preparations.

#### 4. Attempts of direct synthesis of $K_2MnTeO_6$

Two synthesis routes were planned, KMnTe-1 and KMnTe-2, respectively:



In both cases, the reagents were carefully ground together with a mortar and pestle and pressed into pellets. The KMnTe-1 pellet was put into a preheated furnace and held at 450 °C for 1.5 h. Although melting point of  $KNO_3$  was only 336 °C, no signs of melting were visible. The pellet was reground and pressed again. Then, both KMnTe-1 and KMnTe-2 samples were put into the furnace preheated to 650 °C, held for 1.5 h and quenched. XRD patterns of both obtained samples were very similar (Fig. S2a and b) and could not be indexed by analogy with  $Na_2MnTeO_6$  or attributed to any known phase(s). Then, both samples were combined, carefully mixed, divided into two portions and annealed for 3 h at 600 °C (KMnTe-3) or 720 °C (KMnTe-4). However, this did not bring considerable changes according to XRD (Fig. S2c and d). Redox analysis showed significantly reduced oxygen content, i.e., reduction of Mn(4+) and/or Te (6+), with gross compositions  $K_2MnTeO_{5.60}$  and  $K_2MnTeO_{5.64}$  for KMnTi-3 and KMnTi-4, respectively.

Thus, direct synthesis of  $K_2MnTeO_6$  could not be performed under ambient oxygen pressure.

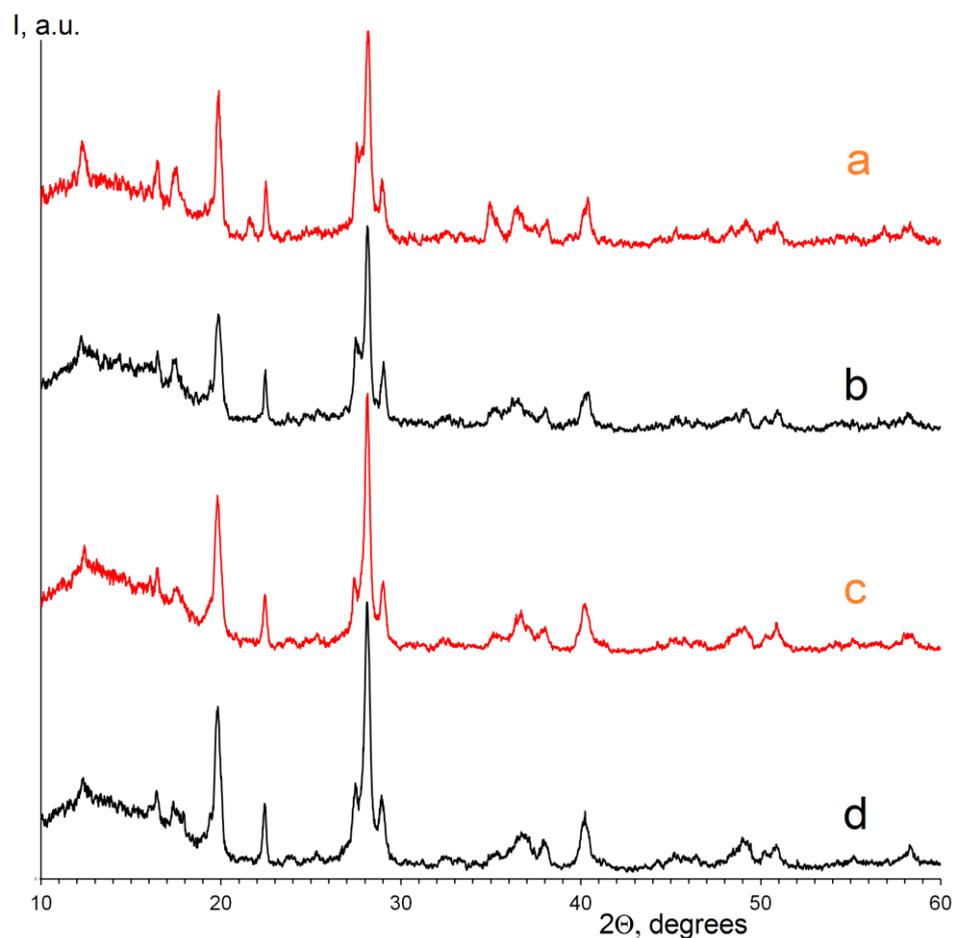


Fig. S2. Room-temperature powder XRD patterns of samples (a) KMnTe-1, 650 °C; (b) KMnTe-2, 650 °C; (c) KMnTe-3, 600 °C; KMnTe-4, 720 °C;

### 5. Attempts of direct synthesis of $\text{Li}_2\text{MnTeO}_6$

First experiments were done with an equimolar mixture  $\text{Li}_2\text{MnO}_3 + \text{TeO}_2$ . It was expected that oxidation in air might result in  $\text{Li}_2\text{MnTeO}_6$ . Calculated weight gain for this process was 5.79 %. Three parallel powder samples, not pressed, were heated shortly at 120 °C to eliminate any moisture that might be adsorbed during mixing, weighed, and then reacted at 500 °C for various periods. After an hour, weight gain was 2.1-2.4% and after 5-6 h it stabilized at the level of 2.70(3) %, i.e., only 47 % of the expected value. Then, the gross formula of the resulting sample LiMnTe-1 should be “ $\text{Li}_2\text{MnTeO}_{5.47}$ ”. Its XRD pattern, rather sharp (Fig. S3a) could not be attributed to any known phase(s), including  $\text{Li}_2\text{MnTeO}_6$  prepared later by ion exchange. Further calcination for 3 h at somewhat higher temperature of 550 °C resulted in essentially same or even slightly reduced weight without considerable changes in the XRD pattern.

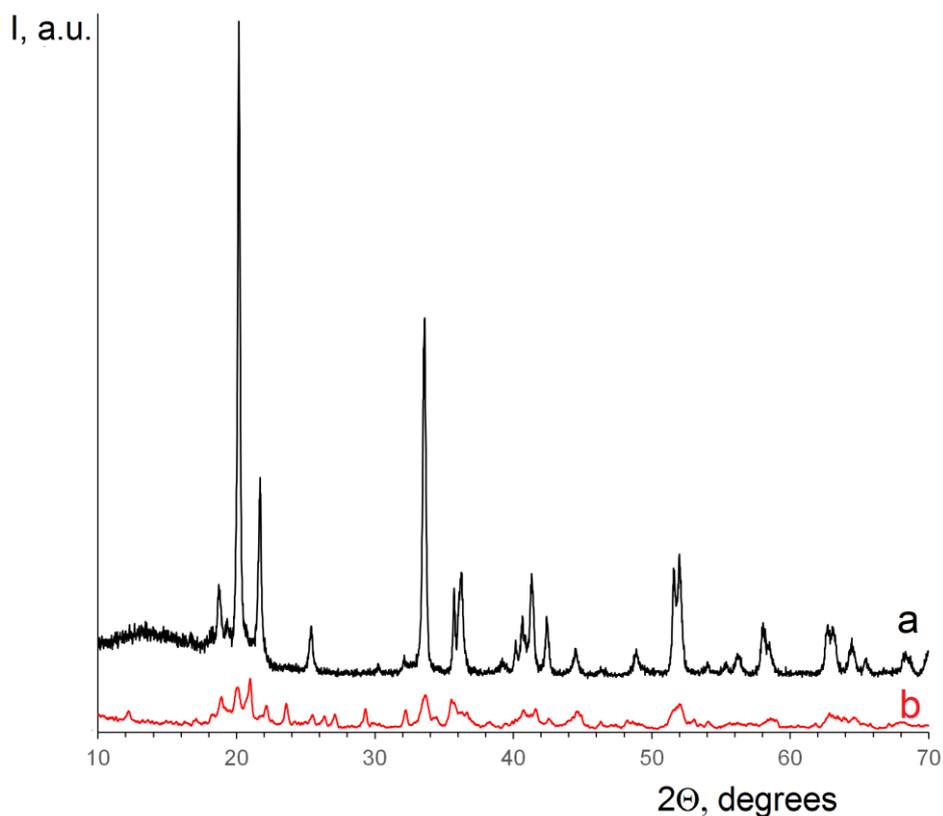


Fig. S3. Room-temperature powder XRD patterns of (a) LiMnTe-1, 500 °C; (b) LiMnTe-2, 450 °C

Then, the preparation was attempted with an equimolar mixture  $\text{Li}_2\text{MnO}_3 + \text{TeO}_3$  that did not need external oxidizer. Thus, the samples might be pressed to enhance contact of particles. The pellets were dried, weighed and heated stepwise. After 6 h at 300 °C, the samples lost 2.97(2) %, corresponding to the gross formula “ $\text{Li}_2\text{MnTeO}_{5.46}$ ”, as in the preceding preparation. However, the weight was not stabilized yet and the very weak XRD pattern of this sample LiMnTe-2 showed mostly reflections from the starting  $\text{Li}_2\text{MnO}_3$ . On further heating at 350, 400, and 450 °C (2-3 h each) weight loss continued and reached 4.4 %. The weak XRD pattern (Fig. S3b) still contained reflections from the starting lithium manganite whereas part of other reflections might be tentatively attributed to a solid solution based on  $\text{LiMn}_2\text{TeO}_6$  (PDF 00-58-532).

Thus, direct synthesis of  $\text{Li}_2\text{MnTeO}_6$  could not be performed under ambient oxygen pressure.

Table S2. Structural data for A<sub>2</sub>MnTeO<sub>6</sub> (A = Li, Na, Ag, Tl)

Partial site inversion, i.e., Mn fraction on Te sites and Te fraction on Mn sites, is denoted as p

A	Li	Na	Ag	Tl	
Formula weight	292.4	324.5	494.3	687.3	
Temperature, K	298	298	300	298	
Step size, °	0.02	0.02	0.02	0.02	
Space group	P $\bar{3}$ 1c	P $\bar{3}$ 1c	P $\bar{3}$ 1c	P $\bar{3}$ 1c	
<i>a</i> , Å	5.01792(7)	5.12127(8)	5.13333(5)	5.11483(8)	
<i>c</i> , Å	9.5289(3)	10.5782(2)	11.16248(20)	14.6639(6)	
<i>V</i> , Å <sup>3</sup>	207.79	240.27	254.74	332.23	
<i>Z</i>	2	2	2	2	
<i>d<sub>X</sub></i> , g/cm <sup>3</sup>	4.67	4.49	6.44	6.87	
Number of <i>hkl</i>	83	88	105	169	
Texture function	March-Dollase, <i>hkl</i> (001) axis				
<i>r</i>	0.9663	0.9512	0.9870	1.0130	
Background treatment	Shifted Chebyshev function of 1st kind, 16–20 terms				
<i>R<sub>p</sub></i>	0.0764	0.0834	0.0693	0.0892	
<i>R<sub>wp</sub></i>	0.1052	0.1119	0.0971	0.1157	
<i>R<sub>exp</sub></i>	0.0828	0.0797	0.0707	0.704	
<i>R<sub>F2</sub></i>	0.02543	0.05606	0.03871	0.05927	
Number of parameters	49	45	51	53	
$\chi^2$	1.61	1.98	1.89	2.70	
Atomic parameters: A	<i>x</i>	2/3	2/3	2/3	
	<i>y</i>	1/3	1/3	1/3	
	<i>z</i>	0.9432(17)	0.96190(32)	0.96333(9)	0.93062(10)
	<i>U<sub>iso</sub></i>	0.0165(5)	0.0415(13)	0.02021 <sup>†</sup>	0.02503(21)
<i>p</i>	0.0590(17)	0	0	0.146(5)	
Atomic parameters: Mn	<i>x</i>	2/3	2/3	2/3	
	<i>y</i>	1/3	1/3	1/3	
	<i>z</i>	1/4	1/4	1/4	1/4
	<i>U<sub>iso</sub></i>	0.0162(5)	0.0095(5)	0.0044(6)	0.0083(12)
Atomic parameters: Te	<i>x</i>	0	0	0	
	<i>y</i>	0	0	0	
	<i>z</i>	1/4	1/4	1/4	1/4
	<i>U<sub>iso</sub></i>	0.02133(19)	0.03766 <sup>†</sup>	0.02115 <sup>†</sup>	0.0188(7)
Atomic parameters: O	<i>x</i>	0.0457(7)	0.0670(7)	0.0590(11)	0.0493(12)
	<i>y</i>	0.6997(7)	0.7148(7)	0.7070(12)	0.7063(12)

<i>z</i>	0.6364(3)	0.6489(3)	0.6556(5)	0.6809(6)
<i>U</i> <sub>iso</sub>	0.0253(12)	0.0341(14)	0.0214(17)	0.026(4)

†Refined anisotropically, *U*<sub>eq</sub> is reported