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Crystal structure of a new polymorphic modification of $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$

<https://doi.org/10.1515/zkri-2019-0038>

Received June 27, 2019; accepted October 8, 2019; published online October 28, 2019

Abstract: The new polymorph of $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$ was prepared via solid state reaction route in a powder form and its crystals were grown by self-flux method. The crystal structure was determined from single crystal X-ray diffraction data. This polymorph crystallizes with an orthorhombic symmetry, space group *Pbca*, with $a=9.8313(4)$, $b=8.7467(3)$, $c=29.6004(11)$ Å, $V=2545.38(17)$ Å³, $Z=8$. Its structure refinement yielded the residual factors $R(F)=0.025$ and $wR(F^2)=0.065$ for 227 parameters and 2605 independent reflections at $2\sigma(I)$ level. The use of group-subgroup schemes in the Bärnighausen formalism enabled an accurate comparison of the *Pbca*- and *Cmc2₁*-polymorphs of $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$. Both polymorphs contain similar $[\text{Mn}_3(\text{SO}_4)_4]^{2-}$ building blocks formed of Mn_2O_{11} dimer units and MnO_5 trigonal pyramids that are interconnected by sharing corners with the SO_4 tetrahedra. However, the stacking of these building blocks along the longest axes of the *Pbca*- and *Cmc2₁*-structures is different. This induces differences in the coordination of the sodium atoms and in the orientation of the SO_4 tetrahedra.

Keywords: polymorphism; self-flux crystal growth method; single crystal structure; sulphate.

Introduction

Polyanionic transition-metal phosphates have been subjected to growing scientific interest as electrode materials for lithium and sodium-ion batteries [1, 2]. Similarly, sulfate salts underwent a true renaissance when interesting electrochemical properties were discovered in sodium iron sulfate compounds. Indeed, the kröhnkite-type $\text{Na}_2\text{Fe}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ [3], the blödite-type $\text{Na}_2\text{Fe}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [4], the alluaudite-type $\text{Na}_{2+2x}\text{Fe}_{2-x}(\text{SO}_4)_3$ [5–7], and the eldfellite-type $\text{NaFe}(\text{SO}_4)_2$ [8] are active in sodium or lithium ion batteries. The sodium manganese sulfate system was

also of interest. Several phases were discovered, such as the vanthoffite-type $\text{Na}_6\text{Mn}(\text{SO}_4)_4$ [9], the glauberite-type $\text{Na}_2\text{Mn}(\text{SO}_4)_2$ [10], the alluaudite-type $\text{Na}_{2+2x}\text{Mn}_{2-x}(\text{SO}_4)_3$ [11, 12], $\text{Na}_{12}\text{Mn}_7(\text{SO}_4)_{13} \cdot 15\text{H}_2\text{O}$ [13], $\text{Na}_2\text{Mn}_{1.167}(\text{SO}_4)_2\text{S}_{0.33}\text{O}_{1.167} \cdot 2\text{H}_2\text{O}$ [10], the kröhnkite-type $\text{Na}_2\text{Mn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ [11], the blödite-type $\text{Na}_2\text{Mn}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [14] and $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$ (1) [15]. The latter compound was prepared at low temperature (450 °C) from a stoichiometric mixture of Na_2SO_4 and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$. It crystallizes in the space group *Cmc2₁* and the unit cell parameters $a_1=14.8307(18)$, $b_1=9.9107(18)$, and $c_1=8.6845(12)$ Å, which can also be transformed to the setting *Bb2₁m* with the unit cell parameters $a_2=9.9107(18)$, $b_2=8.6845(12)$, and $c_2=14.8307(18)$ Å. To differentiate between the unit cell parameters of the $\text{Na}_2\text{M}_3(\text{SO}_4)_4$ compounds ($M=\text{Mg}$ and Mn), these compounds that were prepared by different methods have been attributed a number (n) and the unit cell parameters a_n , b_n , and c_n .

During our search for new positive- and negative-electrodes and solid electrolytes for sodium ion batteries, we have investigated several systems [16–23]. In the binary phase diagram $\text{Na}_2\text{SO}_4\text{--MgSO}_4$, we prepared the compositions $\text{Na}_2\text{Mg}(\text{SO}_4)_2$ and $\text{Na}_2\text{Mg}_2(\text{SO}_4)_3$. Interestingly, during the crystallization of $\text{Na}_2\text{Mg}_2(\text{SO}_4)_3$ at 800 °C single crystals of $\text{Na}_2\text{Mg}_3(\text{SO}_4)_4$ (3) were isolated. This compound crystallizes in the space group *Pbca* with the unit cell parameters $a_3=9.5498(4)$, $b_3=8.7198(3)$ and $c_3=29.2460(11)$ Å. One can clearly notice that a_3 , b_3 and c_3 are similar to a_2 , b_2 and $2 \times c_2$, respectively. This is clearly a hint on the possible existence of polymorphic modifications in these compounds. Therefore, we decided to replace gradually Mg by Mn in order to prepare the *Pbca*-polymorph of $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$ which might be of interest as a positive electrode for sodium ion batteries. During the crystallization of the compounds $\text{Na}_2\text{Mg}_2\text{Mn}(\text{SO}_4)_4$, $\text{Na}_2\text{MgMn}_2(\text{SO}_4)_4$ and $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$ at 800 °C, single crystals of *Pbca*- $\text{Na}_2\text{Mg}_{2.5}\text{Mn}_{0.5}(\text{SO}_4)_4$ (4), *Pbca*- $\text{Na}_2\text{Mg}_{1.5}\text{Mn}_{1.5}(\text{SO}_4)_4$ (5) and *Pbca*- $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$ (6) were isolated, respectively. Their crystal structures and compositions were determined from single crystal X-ray diffraction data. The three compounds are isostructural with *Pbca*- $\text{Na}_2\text{Mg}_3(\text{SO}_4)_4$ (3). Their unit cell parameters are given in the Tables S1 and S2.

Since we realized that Dr. Slater had already published the crystal structure of $\text{Na}_2\text{Mg}_3(\text{SO}_4)_4$ (7) [24], herein we report on mainly the crystal structure of the new polymorph *Pbca*- $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$ (6) based on single

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crystals X-ray diffraction data. Furthermore, we discuss its structural relationship with the known polymorph $\text{Cmc}2_1\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$ using complex group-subgroup schemes in the Bärnighausen formalism.

Experimental section

Synthesis

The title compound $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$ was prepared by a solid state reaction route, from a stoichiometric mixture of Na_2SO_4 (Aldrich, 99.5%) and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Merck, 99.9%). 0.298 g and 1.046 g of the starting materials, respectively were ground in an agate mortar then pelletized and put into platinum crucible and heated at 600 °C for 12 h in Argon. The progress of the reaction was followed by powder X-ray diffraction (PXRD) and the beige powder sample was pure. The single crystals were then obtained using self-flux method. A stoichiometric mixture of Na_2SO_4 and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was heated at 800 °C for 12 h then quenched to room temperature. This led mainly to colourless crystals of $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$ besides few crystals of Na_2SO_4 .

The compositions $\text{Na}_2\text{Mg}_2\text{Mn}(\text{SO}_4)_4$ and $\text{Na}_2\text{MgMn}_2(\text{SO}_4)_4$ were prepared by a solid state reaction route, from a stoichiometric mixture of Na_2SO_4 (Aldrich, 99.5%), MgSO_4 (Merck, 99.9%) and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Merck, 99.9%). The two samples were heated at 600 °C for 12 h and at 800 °C for 10 h in Argon. This led to the formation of $\text{Pbca-Na}_2\text{Mg}_{2.5}\text{Mn}_{0.5}(\text{SO}_4)_4$ (4) and $\text{Pbca-Na}_2\text{Mg}_{1.5}\text{Mn}_{1.5}(\text{SO}_4)_4$ (5) single crystals, respectively.

Powder X-ray diffraction measurements

To ensure the purity of $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$ powder, routine PXRD measurements were performed. The data were collected at room temperature over the 2θ angle range of $5^\circ \leq 2\theta \leq 75^\circ$ with a step size of 0.01° using a Bruker D8 advance diffractometer operating with $\text{CuK}\alpha$ radiation (Bruker, Darmstadt, Germany). Full pattern matching refinement was performed with the Jana2006 program package (Institute of Physics, Prague, Czech Republic) [25]. The background was estimated by a Legendre function and the peak shapes were described by a pseudo-Voigt function.

Single crystal X-ray diffraction measurements

$\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$ (6), $\text{Pbca-Na}_2\text{Mg}_{2.5}\text{Mn}_{0.5}(\text{SO}_4)_4$ (4) and $\text{Pbca-Na}_2\text{Mg}_{1.5}\text{Mn}_{1.5}(\text{SO}_4)_4$ (5) single crystals suitable for single crystal X-ray diffraction were selected on the basis of the size and the sharpness of the diffraction spots. The data collections were carried out on a Bruker D8 Venture diffractometer using $\text{MoK}\alpha$ radiation. Data processing and all refinements were performed with the APEX3 and JANA2006 program packages, respectively [25, 26]. For the data collection details, see Tables 1 and S1. Further details on the structure refinements of $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$, $\text{Na}_2\text{Mg}_{1.5}\text{Mn}_{1.5}(\text{SO}_4)_4$, $\text{Na}_2\text{Mg}_{2.5}\text{Mn}_{0.5}(\text{SO}_4)_4$, and $\text{Na}_2\text{Mg}_3(\text{SO}_4)_4$ may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD–1936610–1936613.

Tab. 1: Crystallographic data and structure refinement for $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$.

Crystal data	
Chemical formula	$\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$
M_r	595
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
Temperature (K)	293
a, b, c (Å)	9.8313(4), 8.7467(3), 29.6004(11)
V (Å ³)	2545.38(17)
Z	8
Radiation type	$\text{Mo K}\alpha$
μ (mm ^{−1})	3.75
Crystal size (mm)	$0.47 \times 0.08 \times 0.04$
Data collection	
Diffractometer	D8 Venture
Absorption correction	Multi-scan
SADABS	
$T_{\min}, T_{\max}$	0.593, 0.747
No. of measured reflections	18,976
No. of independent reflections	3151
No. of observed reflections	2605 [$I > 2\sigma(I)$]
R_{int}	0.033
$(\sin \theta / \lambda)_{\max}$ (Å ^{−1})	0.666
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.025, 0.065, 1.14
No. of reflections	3151
No. of parameters	227
No. of restraints	0
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ^{−3})	0.38, −0.31

Electron microprobe analysis

Semiquantitative energy-dispersive X-ray spectroscopy (EDX) analyses of different single crystals including the ones investigated on the diffractometer were carried out with a 7610F (JEOL) scanning electron microscope (SEM). Although the crystals were beam sensitive, the experimentally observed compositions were close to the ideal one of $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$.

Results and discussion

Structure refinement

The systematic absences observed for $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$ agree with the *Pbca* space group. Atomic positions of the majority of atoms were found by the Superflip program implemented in JANA2006 program package [25, 27]. The use of the difference Fourier synthesis allowed us to localize the remaining oxygen atomic positions. With anisotropic atomic displacement parameters (ADPs), the final residual factors converged

to the values $R(F)=0.025$ and $wR(F^2)=0.0650$ for 227 refined parameters, 3151 independent reflections and difference-Fourier residues in the range between -0.38 and $+0.31 \text{ e}\text{\AA}^{-3}$. The refined atomic positions and ADPs are given in Tables 2 and S3, respectively. The EDX elemental analyses performed on the crystal used for the data collection confirmed the composition $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$ (Figure 1). Furthermore, using the crystallographic data obtained by the single crystal XRD, the X-ray powder pattern of $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$ (8) could be fully indexed which confirmed the formation of this sample (Figure 2). The refined unit cell parameters were $a_8=9.9111(3)$, $b_8=8.7065(3)$, and $c_8=29.6932(10) \text{ \AA}$. One should mention that it is not excluded that this sample could be a mixture of both polymorphs.

The crystal structures of $\text{Pbca-Na}_2\text{Mg}_{2.5}\text{Mn}_{0.5}(\text{SO}_4)_4$ (4) and $\text{Pbca-Na}_2\text{Mg}_{1.5}\text{Mn}_{1.5}(\text{SO}_4)_4$ (5) were refined using the same procedure as for $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$ (6). The refinement of the occupancies of the manganese atoms showed a significant decrease consequently, Mn/Mg statistical disorders were introduced and restrictions on their ADPs were applied. The refined atomic positions and ADPs are given in Tables S4 and S5, respectively.

Tab. 2: Fractional atom coordinates and isotropic atomic displacement parameters ($\text{\AA}^2$) for $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$.

Atom	Wyck.	x	y	z	Ueq ($\text{\AA}^2$)
Na1	8c	0.45388(10)	-0.12394(11)	0.69154(3)	0.0211(3)
Na2	8c	0.40639(12)	0.92439(12)	0.55287(4)	0.0315(4)
Mn1	8c	0.85011(3)	-0.07081(4)	0.69589(1)	0.01166(11)
Mn2	8c	0.68455(4)	0.43074(4)	0.55205(1)	0.01420(11)
Mn3	8c	0.32662(4)	0.25433(4)	0.62627(1)	0.01423(11)
S1	8c	0.36779(5)	0.22999(6)	0.73526(2)	0.00833(15)
O1	8c	0.31892(16)	0.30762(19)	0.77584(5)	0.0158(5)
O2	8c	0.50865(16)	0.27808(19)	0.72723(6)	0.0179(5)
O3	8c	0.36487(16)	0.06367(17)	0.74200(5)	0.0147(5)
O4	8c	0.28144(16)	0.27024(19)	0.69614(5)	0.0158(5)
S2	8c	0.44398(5)	0.59764(6)	0.62045(2)	0.00955(15)
O5	8c	0.50687(17)	0.58284(19)	0.66480(5)	0.0205(5)
O6	8c	0.32541(17)	0.4938(2)	0.61729(6)	0.0207(6)
O7	8c	0.38987(17)	0.75595(17)	0.61640(5)	0.0142(5)
O8	8c	0.53850(17)	0.56973(19)	0.58405(6)	0.0234(6)
S3	8c	0.61905(6)	0.12227(6)	0.62812(2)	0.00922(15)
O9	8c	0.6340(2)	0.29033(19)	0.62759(6)	0.0261(6)
O10	8c	0.65967(17)	0.0609(2)	0.58450(6)	0.0246(6)
O11	8c	0.69495(18)	0.0558(2)	0.66506(6)	0.0249(6)
O12	8c	0.47360(16)	0.0860(2)	0.63575(6)	0.0205(5)
S4	8c	0.39288(6)	0.27110(6)	0.51362(2)	0.00971(15)
O13	8c	0.31187(16)	0.40863(18)	0.50557(6)	0.0177(5)
O14	8c	0.37040(16)	0.15742(18)	0.47753(5)	0.0168(5)
O15	8c	0.53949(16)	0.30299(18)	0.51469(5)	0.0184(5)
O16	8c	0.34954(18)	0.2017(2)	0.55640(5)	0.0211(5)

Fig. 1: Image and EDX analysis of the $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$ single crystal used for the data collection. The circle represents the area where the EDX analysis was performed.

Fig. 2: Observed, calculated and difference plots for PXRD ($\text{Cu-K}\alpha$ radiation) refinement of $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$.

Crystal structure

$\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$ (6) is a new polymorph of $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$. Its structure contains a buildup of Mn_2O_{11} dimer units and

MnO_5 trigonal pyramids. The latter ones are interconnected by sharing corners with the SO_4 tetrahedra leaving cavities in which two symmetry different sodium atoms are located (Figure 3a). Selected interatomic distances are given in Table 3.

In $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$, the manganese atoms occupy three different atomic positions. Mn1 and Mn2 are coordinated by six oxygen atoms forming strongly distorted octahedra that share a corner and form a Mn_2O_{11} dimer unit (Figure 4a) with Mn1–O distances ranging from 2.0945(18) to 2.3635(17) Å and Mn2–O distances ranging from 2.1063(17) to 2.5991(17) Å (Table 3). Mn3 is coordinated by five oxygen atoms forming a trigonal bipyramid with the Mn3–O distances ranging from 2.0818(17) to 2.1484(17) Å (Figure 4c). The average distances of 2.1783 and 2.2238 Å for Mn1–O and Mn2–O, respectively are in good agreement with the sum of the effective ionic radii of the high spin Mn^{2+} and O^{2-} [$\text{IR}_{(\text{Mn}^{2+})} + \text{IR}_{(\text{O}^{2-})} = 0.83 + 1.4$ Å] [29]. The Mn_2O_{11} dimer units and the MnO_5 trigonal bipyramids are interconnected through four different SO_4 tetrahedra. In the S1O_4 and S4O_4 tetrahedra the S–O distances are very similar, whereas in the S2O_4 and S3O_4 tetrahedra short and stretched S–O distances are observed (see Table 3). The distances $d(\text{S–O})_{\min}$ and $d(\text{S–O})_{\max}$ of 1.4436(18) and 1.4882(16) Å, respectively are slightly shorter than the sum of the effective ionic radii of S^{6+} and O^{2-} [$\text{IR}_{(\text{S}^{6+})} + \text{IR}_{(\text{O}^{2-})} = 0.12 + 1.38$ Å] [29].

The title compound contains two different sodium atoms Na1 and Na2. Na1 is coordinated by seven oxygen atoms forming a strongly distorted capped-trigonal-prism with Na1–O distances ranging from 2.3853(18) to 2.7341(19) Å and with an average Na1–O distance of 2.531 Å and a bond valence sums (BVS) of 1.01 (Figure 4e). For Na2 the coordination sphere is not well defined. Even when the coordination sphere is increased to 3.2 Å, Na2 remains

underbonded with a BVS of 0.9. The BVS values of 2.15, 2.02, 2.06, 6.09, 6.12, 6.16 and 6.09 are in agreement with the expected value of +2 and +6 for Mn1^{+2} , Mn2^{+2} , Mn3^{+2} , S1^{+6} , S2^{+6} , S3^{+6} and S4^{+6} , respectively [28].

Comparison of $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$ and $\text{Bb2}_1m\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$

The crystal structures of $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$ and $\text{Bb2}_1m\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$ are given in Figures 3a and b, respectively. Although both structures are different, one observes common features that can be listed below:

1. In $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$ the cell parameters a_6 , b_6 and c_6 are almost equal to a_2 , b_2 and $2 \times c_2$ in $\text{Bb2}_1m\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$, respectively (Figure 3),
2. Mn_2O_{11} dimer units are present in both compounds. Only a slight difference in the interatomic distances is observed (Figures 4a and b),
3. MnO_5 trigonal-bipyramids are present in both compounds (Figures 4c and d). If we consider the stretched distances $d_{\text{Mn3–O6}}$ in $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$ and $d_{\text{Mn2–O8}}$ in $\text{Bb2}_1m\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$, the isolated trigonal-bipyramids would be transformed to an infinite chain of corner-sharing octahedra,
4. The Mn_2O_{11} dimer units and the MnO_5 trigonal bipyramids are interconnected through SO_4 tetrahedra which are slightly tilted in $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$ in comparison to the tetrahedra in $\text{Bb2}_1m\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$ (Figure 5),
5. The coordination of Na1 in both compounds is similar (Figures 4e and f), and
6. The theoretical powder X-ray diffraction patterns are similar (Figure S1). Only few additional peaks were observed for $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$.

Fig. 3: Perspective view of the crystal structures of $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$ (a) and $\text{Bb2}_1m\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$ (b). Only the polyhedra around the Mn and S atoms were drawn.

Tab. 3: Interatomic distances (in Å) and bond valence sums (BVS) for $Pbca\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$ and $Bb2_1m\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$.

$Pbca\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$				$Bb2_1m\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$	
Distances		Distances		Distances	
Na1–O3	2.3853(18)	Mn1–O11	2.0945(18)	Na1–O10	2.283(4)
Na1–O12	2.478(2)	Mn1–O2	2.1297(17)	Na1–O7	2.330(3)
Na1–O4	2.4955(19)	Mn1–O1	2.1431(16)	Na1–O9	2.415(4)
Na1–O1	2.5060(18)	Mn1–O5	2.1517(17)	Na1–O1	2.619(4)
Na1–O7	2.5390(18)	Mn1–O3	2.1874(16)	Na1–O5	2.637(4)
Na1–O2	2.5790(19)	Mn1–O9	2.3635(17)	Na1–O3	2.650(4)
Na1–O5	2.7341(19)		<2.1783>		<2.489>
	<2.531>		^a 2.154(4) [6]		1.022 [6]
	^a 1.013(2) [7]	Mn2–O8	2.1063(17)	Mn1–O4	2.095(3)
Na2–O7	2.3944(18)	Mn2–O15	2.1226(16)	Mn1–O9	2.096(3)
Na2–O14	2.4774(19)	Mn2–O10	2.1364(18)	Mn1–O5	2.161(3)
Na2–O16	2.492(2)	Mn2–O14	2.1679(16)	Mn1–O1	2.171(3)
Na2–O13	2.5658(19)	Mn2–O13	2.2102(17)	Mn1–O10	2.216(3)
Na2–O15	2.8703(19)	Mn2–O9	2.5991(17)	Mn1–O6	2.408(2)
Na2–O12	2.907(2)		<2.2238>		<2.1911>
Na2–O10	2.916(2)		^a 2.018(4) [6]		^a 2.103(8) [6]
Na2–O6	3.033(2)	Mn3–O12	2.0818(17)	Mn2–O2	2.082(4)
Na2–O14	3.0420(19)	Mn3–O6	2.1113(18)	Mn2–O3 (×2)	2.123(3)
Na2–O16	3.183(2)	Mn3–O4	2.1198(15)	Mn2–O8	2.161(5)
	<2.788>	Mn3–O16	2.1309(16)	Mn2–O7	2.174(4)
	^a 0.8975(18) [10]	Mn3–O7	2.1484(17)	Mn2–O8	2.557(5)
			<2.1184>		<2.1326>
S1–O1	1.4611(16)		^a 2.062(4) [5]		^a 1.988(10) [5]
S1–O2	1.4667(17)	S3–O11	1.4456(19)		
S1–O3	1.4687(16)	S3–O10	1.4543(19)		
S1–O4	1.4782(16)	S3–O9	1.4773(18)		
	<1.4686>	S3–O12	1.4819(17)		
	^a 6.087(13) [4]		<1.4648>		
S2–O8	1.4436(18)		^a 6.156(15) [4]		
S2–O5	1.4569(17)	S4–O13	1.4622(17)		
S2–O6	1.4808(18)	S4–O16	1.4673(17)		
S2–O7	1.4882(16)	S4–O15	1.4684(16)		
	<1.4674>	S4–O14	1.4761(16)		
	^a 6.115(14) [4]		<1.4685>		
			^a 6.090(14) [4]		

Average distances are given in <> and coordination numbers are given in []. ^aBond valence sum, B.V. = $e^{(r_0-r)/b}$ with the following parameters: $b = 0.37$, $r_0(\text{Na}^{\text{I}}-\text{O}) = 1.803$, $r_0(\text{Mn}^{\text{II}}-\text{O}) = 1.790$, and $r_0(\text{S}^{\text{VI}}-\text{O}) = 1.624$ Å [28].

All the similarities mentioned above indicate that there is a strong structural relationship between both polymorphs. For an accurate comparison of $Bb2_1m\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$ [$a2 = 9.9107(18)$, $b2 = 8.6845(12)$, and $c2 = 14.8307(18)$ Å] and $Pbca\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$ [$a6 = 9.8313(4)$, $b6 = 8.7467(3)$ and $c6 = 29.6004(11)$ Å], it is necessary to find a supercell, common to both structures, in which the comparison of the atomic position would be simple. For this purpose, the use of group-subgroup schemes in the Bärnighausen formalism is the key [30–32]. After different transformations, the $Pbca\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$ and $Bb2_1m\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$ cells were transformed to the new supercells (SC-I) and (SC-II),

respectively, which are depicted in Figures 6a and b. The unit cell of $Pbca\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$ and (SC-I) are identical whereas, the supercell (SC-II) was obtained by doubling the $Bb2_1m\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$ unit cell along the c axis. Details on these transformations are given in Supplementary Information.

The software Compstru from Bilbao Crystallographic Server (Bilbao, Spain) is often used to compare crystal structures of the same symmetry, however it failed to compare SC-I and SC-II which indicates that the atomic positions in both structures are different. To confirm that, each supercell was divided into five sections parallel to the c axis. The supercell SC-I can be described

Fig. 4: Coordination polyhedra of the manganese and sodium atoms in the compounds $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$ (a, c, e) and $\text{Bb2}_1\text{m-Na}_2\text{Mn}_3(\text{SO}_4)_4$ (b, d, f).

Fig. 5: The connectivity between the Mn_2O_{11} dimer units, the MnO_5 trigonal bipyramids and the SO_4 tetrahedra in $\text{Pbca-Na}_2\text{Mn}_3(\text{SO}_4)_4$ (a) and $\text{Bb2}_1\text{m-Na}_2\text{Mn}_3(\text{SO}_4)_4$ (b).

as a stacking of the sections $\text{A}_{\text{SC-I}}$, $\text{B}_{\text{SC-I}}$, $\text{C}_{\text{SC-I}}$, $\text{D}_{\text{SC-I}}$, $\text{A}_{\text{SC-I}}$ (Figure 6a) with the sections $\text{C}_{\text{SC-I}}$ and $\text{D}_{\text{SC-I}}$ related by symmetry elements to the sections $\text{A}_{\text{SC-I}}$ and $\text{B}_{\text{SC-I}}$, respectively. On the other hand, the supercell SC-II results from the stacking of the sections $\text{A}_{\text{SC-II}}$, $\text{B}_{\text{SC-II}}$, $\text{A}_{\text{SC-II}}$, $\text{B}_{\text{SC-II}}$, $\text{A}_{\text{SC-II}}$ (Figure 6b). It should be noted that the structures should not be considered as layered structures. Dividing the supercells to five sections was performed only to ease the visual comparison of the two structures. Indeed, although the projection views along the b axis of SC-I and SC-II are very similar, the projection views along the c axis of the sections of SC-I and SC-II emphasize several differences (see

the sections $\text{C}_{\text{SC-I}}$, $\text{D}_{\text{SC-I}}$ and $\text{A}_{\text{SC-II}}$, $\text{B}_{\text{SC-II}}$). The sections $\text{A}_{\text{SC-I}}$ and $\text{B}_{\text{SC-I}}$ are almost identical to the sections $\text{A}_{\text{SC-II}}$ and $\text{B}_{\text{SC-II}}$, respectively. The SO_4 tetrahedra in SC-I are slightly tilted when compared to the tetrahedra in SC-II.

Comparison of the $\text{Pbca-Na}_2\text{Mn}_{3-x}\text{Mg}_x(\text{SO}_4)_4$ compounds

Starting from the composition $\text{Na}_2\text{Mg}_3(\text{SO}_4)_4$, the total replacement of the Mg by Mn atoms was possible and led to an increase of the cell volume from $2435.38(16) \text{ \AA}^3$ to

Fig. 6: Projection view along the b axis of the crystal structures of $Pbca\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$ (a) and $Cmc2_1\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$ (b) after the transformations to supercells with $P1$ space group. Projection views along the c axis of different sections are given for comparison. Only the polyhedra around the Mn and S atoms were drawn.

2545.38(17) Å³ of $Pbca\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$. The structure did not change, which confirms the existence of a full solid solution between $\text{Na}_2\text{Mg}_3(\text{SO}_4)_4$ and $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$. In the intermediate phases $\text{Na}_2\text{Mg}_{2.5}\text{Mn}_{0.5}(\text{SO}_4)_4$ and $\text{Na}_2\text{Mg}_{1.5}\text{Mn}_{1.5}(\text{SO}_4)_4$ a Mg/Mn statistical disorder was observed in all the Mg sites (Table S4). Using the program Compstru, we investigated and quantified the degree of similarities between the structures of $Pbca\text{-Na}_2\text{Mn}_3(\text{SO}_4)_4$, $Pbca\text{-Na}_2\text{Mg}_{2.5}\text{Mn}_{0.5}(\text{SO}_4)_4$, $Pbca\text{-Na}_2\text{Mg}_{1.5}\text{Mn}_{1.5}(\text{SO}_4)_4$ and $Pbca\text{-Na}_2\text{Mg}_3(\text{SO}_4)_4$ [33–36]. Our results that are presented in the Tables S6–S8 confirm that the four compounds are isostructural.

Conclusion

During the investigation of the binary phase diagram $\text{Na}_2\text{SO}_4\text{--MgSO}_4$ and the crystallization of $\text{Na}_2\text{Mg}_2(\text{SO}_4)_3$, single crystals of $\text{Na}_2\text{Mg}_3(\text{SO}_4)_4$ were isolated. Thereafter, the Mg atoms were gradually replaced by Mn and single crystals of three new compounds could be grown using self-flux method. Interestingly, the four prepared compounds $\text{Na}_2\text{Mg}_3(\text{SO}_4)_4$,

$\text{Na}_2\text{Mg}_{2.5}\text{Mn}_{0.5}(\text{SO}_4)_4$, $\text{Na}_2\text{Mg}_{1.5}\text{Mn}_{1.5}(\text{SO}_4)_4$ and $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$ are isostructural and crystallize in the space group $Pbca$ which confirms the existence of a full solid solution between $\text{Na}_2\text{Mg}_3(\text{SO}_4)_4$ and $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$ and the existence of a second polymorphic modification of $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$. It should be mentioned that the previously described polymorph of $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$ crystallizes in the space group $Cmc2_1$ ($Bb2_1m$). The use of group-subgroup schemes in the Bärnighausen formalism enabled an accurate structural comparison of the $Pbca$ - and $Cmc2_1$ -polymorphs of $\text{Na}_2\text{Mn}_3(\text{SO}_4)_4$. Although, the crystal structures of both polymorphs are different, they share similar features: they contain the same building blocks Mn_2O_{11} dimer units and MnO_5 trigonal pyramids that are interconnected by sharing corners with the SO_4 tetrahedra.

Acknowledgements: Authors would like to thank Dr. Said Mansour for giving us access to the characterization tools in the core lab. The authors also would like to thank the reviewers who have made substantial efforts to improve the article. The publication of this article was funded by the Qatar National Library.

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Supplementary Material: The online version of this article offers supplementary material (<https://doi.org/10.1515/zkri-2019-0038>).