Hamdi Ben Yahia* and Masahiro Shikano

Structural properties of the alluaudite-type materials $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ ($x = 0.62$ and 1.85)

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Abstract: The new members of the $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ ($0 \leq x \leq 2$) solid solution were synthesized by a solid-state reaction route. The crystal structures of $\text{Ag}_{1.38}\text{Na}_{0.62}\text{Mn}_3(\text{VO}_4)_3$ ($x = 0.62$) and $\text{Ag}_{0.15}\text{Na}_{1.85}\text{Mn}_3(\text{VO}_4)_3$ ($x = 1.85$) were solved using single crystal X-ray diffraction. These phases crystallize with a monoclinic symmetry (space group $C2/c$), and their structures are new members of the well-known alluaudite family. In both compounds, the Ag^+/Na^+ , $\text{Mn}^{2+}/\text{Mn}^{3+}$ and V^{5+} cations are eight-, six-, and four-coordinated to oxygen atoms, respectively. All the atoms are perfectly ordered except for the Ag and Na atoms which are statistically disordered over a $4b$ and a $4e$ atomic position. This single-crystal structural study confirms the existence of a full solid solution $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ ($0 \leq x \leq 1.85$).

Keywords: crystal structure; solid solution; vanadate.

1 Introduction

Lithium-ion batteries are commonly used for portable electronics, military and aerospace applications and electric vehicles (EVs). Due to the global warming, an increase in the sales of EVs is observed and is expected to continue to rise in the next years. This has induced a significant increase in the price of lithium (up to 3 times in 1 year) and researchers are afraid that the increasing demand may cause disruption in the raw material supply chain in the future. Consequently, they are seriously thinking of developing sodium-ion batteries (NIBs) since sodium is one of the most abundant and cheap elements on earth. Several sodium iron-based materials have already been investigated as possible electrodes for NIBs [1–15].

The alluaudite compounds with the general formula $\text{AA}'\text{MM}'_2(\text{XO}_4)_3$ ($A = \text{Li}, \text{Na}$; $M = \text{Mn}, \text{Fe}$; and $X = \text{S}, \text{P}$) have been particularly chosen because they are expected to be low cost materials, safe and with relatively high energy density. Indeed, the electrochemical properties of several alluaudite phosphates $\text{Na}_2\text{M}_2\text{Fe}(\text{PO}_4)_3$ ($M = \text{Mn}, \text{Fe}, \text{Co}$, and Ni) [7, 16, 17] and sulfates $\text{Na}_{2+x}\text{M}_{2-y}(\text{SO}_4)_3$ ($M = \text{Mn}$ and Fe) [18, 19] were studied. Among these materials, perhaps $\text{Na}_{2+x}\text{Fe}_{2-y}(\text{SO}_4)_3$ is the most interesting for NIBs since it operates at a relatively high voltage of 3.8 V (vs. Na). To our knowledge, no alluaudite vanadates were reported so far as electrodes for Li- or Na-ion batteries, except $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_2\text{Fe}(\text{VO}_4)_3$ [20]. These materials have shown higher ionic conductivities as compared to the homologous phosphates. Furthermore, $\text{Na}_2\text{Mn}_2\text{Fe}(\text{VO}_4)_3$ was shown to be active in Na-ion batteries, however due to the large size of the particles a huge polarization was observed and the cyclability was poor.

Since we have recently successfully prepared the first alluaudite vanadate containing silver, $\text{Ag}_2\text{Mn}_3(\text{VO}_4)_3$ [21], we decided to gradually replace the silver by sodium atoms in order to get $\text{Na}_2\text{Mn}_3(\text{VO}_4)_3$ with the alluaudite-type structure which might be interesting as electrode material for sodium ion batteries. Herein we report on the crystal growth of $\text{Ag}_{1.38}\text{Na}_{0.62}\text{Mn}_3(\text{VO}_4)_3$ ($x = 0.62$) and $\text{Ag}_{0.15}\text{Na}_{1.85}\text{Mn}_3(\text{VO}_4)_3$ ($x = 1.85$) and their crystal structures which have been determined from single-crystal X-ray diffraction data.

2 Experimental section

2.1 Synthesis

The new compounds $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ ($x = 1/2, 1, 3/2, 19/10$, and 2) were prepared by a solid-state reaction route from a stoichiometric mixture of Ag_2O , Na_2CO_3 , MnO , Mn_2O_3 , and V_2O_5 . The mixtures were ground, pelletized and fired at 460°C for 8 h under argon. After grinding a further heating of the mixtures at $T = 460^\circ\text{C}$ for 18 h led to the formation of mainly the alluaudite phases besides few unidentified impurities. Different treatments (time and temperature) did not improve the results. When the pellets of ($x = 1, 1.9$, and 2) were melted above 700°C , decompositions of the

*Corresponding author: Hamdi Ben Yahia, Qatar Environment and Energy Research Institute (QEERI 2.0), Hamad Bin Khalifa University, Qatar Foundation, P. O. Box 34110, Doha, Qatar, Phone: +974-4454-7762, Fax: +974-4454 0547, E-mail: hyahia@qf.org.qa

Masahiro Shikano: Research Institute of Electrochemical Energy, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

phases ($x=1.9$ and 2) were observed, whereas large black single crystals of the alluaudite phase were obtained for ($x=1$) (Fig. S1; supporting information available online). Consequently, for ($x=1.9$) tiny black single crystals were grown by sintering the corresponding pellet slightly below the melting point for a period of 3 weeks (Fig. S1). This procedure was repeated for ($x=2$) but was not successful. Single crystals of $\text{NaMn}_4(\text{VO}_4)_3$ were often obtained after the melting of the composition $\text{Na}_2\text{Mn}_3(\text{VO}_4)_3$.

2.2 Electron microprobe analysis

Semiquantitative EDX analyses of different single crystals including the ones investigated on the diffractometer were carried out with an Oxford EDS system installed on a Jeol 7610F scanning electron microscope (SEM). The experimentally observed compositions were close to the ideal one for ($x=1.9$), however for ($x=1$) the compositions varied significantly from $\text{Ag}_{2/3}\text{Na}_{4/3}\text{Mn}_3(\text{VO}_4)_3$ to $\text{Ag}_{4/3}\text{Na}_{2/3}\text{Mn}_3(\text{VO}_4)_3$.

2.3 X-ray diffraction measurements

To check the formation of the $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ phases ($x=1/2, 1, 3/2, 1.9$, and 2), routine powder XRD measurements were performed. The data were collected at room temperature over the 2θ angle range $10 \leq 2\theta \leq 80^\circ$ with a step size of 0.01° using a D8 advance Bruker diffractometer operating with $\text{CuK}\alpha$ radiation.

Single crystals of $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ ($x=0.62$ and 1.85) suitable for XRD were selected on the basis of the size and the sharpness of the diffraction spots. The data collections were carried out on a D8 venture (Bruker) diffractometer using $\text{MoK}\alpha$ radiation. Data processing and all refinements were performed with the APEX3 program package. Gaussian-type absorption corrections were applied and the crystal shapes were determined with the video microscope (Fig. S1). For data collection details, see Table 1. One should mention that the single crystals of $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ ($x=0.62$ and 1.85) used for the data collection were obtained from the crystallization of the powders of compositions ($x=1$ and 1.9), respectively.

Table 1: Crystallographic data and structure refinement of $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ ($x=0.62$ and 1.85).

Crystal data	$\text{Ag}_{1.377}\text{Na}_{0.623}\text{Mn}_3\text{V}_3\text{O}_{12}$	$\text{Ag}_{0.152}\text{Na}_{1.848}\text{Mn}_3\text{V}_3\text{O}_{12}$
Chemical formula	$\text{Ag}_{1.377}\text{Na}_{0.623}\text{Mn}_3\text{V}_3\text{O}_{12}$	$\text{Ag}_{0.152}\text{Na}_{1.848}\text{Mn}_3\text{V}_3\text{O}_{12}$
M_r	672.5	568.5
Crystal system, space group	Monoclinic, $C2/c$	Monoclinic, $C2/c$
Temperature, K	293	293
A , Å	12.1124(19)	11.895(2)
B , Å	13.1761(19)	13.126(2)
C , Å	6.9043(12)	6.8361(12)
β , deg	112.153(3)	111.767(3)
V , Å ³	1020.5(3)	991.2(3)
Z	4	4
Radiation type	$\text{MoK}\alpha$	$\text{MoK}\alpha$
μ , mm ⁻¹	8.9	6.9
Crystal size, mm ³	$0.038 \times 0.06 \times 0.19$	$0.08 \times 0.05 \times 0.03$
Density, g cm ⁻³	4.38	3.81
Data collection		
Diffractometer	Smart Apex	Smart Apex
Absorption correction	Gaussian	Gaussian
$T_{\min}/T_{\max}$	0.183/0.694	0.689/0.803
No. of measured reflections	2760	2777
No. of independent reflections	860	1120
No. of observed reflections	702 [$I > 3 \sigma(I)$]	1111 [$I > 0 \sigma(I)$]
R_{int}	0.082	0.023
$(\sin \theta / \lambda)_{\max}$, Å ⁻¹	0.058	0.658
Refinement		
R [$F^2 > 2 \sigma(F^2)$]/ $wR(F^2)$	0.032/0.082	0.035/0.067
GoF (S)	1.18	1.09
No. of reflections	860	1120
No. of parameters	97	97
$\Delta\rho_{\max/\min}$, e Å ⁻³	0.98/−1.03	0.39/−0.47

CCDC 1946641 and 1946642 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3 Results and discussion

3.1 Structure refinement

3.1.1 Powder X-ray diffraction

To check the purity of our samples, full pattern matching refinements were performed with the JANA2006 program package [22]. The backgrounds were estimated by a Legendre function, and the peak shapes were described by a pseudo-Voigt function. The obtained cell parameters are given in Table 2. When the sodium atoms ($R_{\text{ionic}} = 1.18 \text{ \AA}$) were replaced by silver atoms ($R_{\text{ionic}} = 1.28 \text{ \AA}$) the b cell parameter and the cell volume decreased from 13.2079 to 13.0232 $\text{\AA}$ and from 997.07 to 988.42 $\text{\AA}^3$, respectively, and the β angle increased from 111.408 to 111.668°. Furthermore, no significant changes of the cell parameters a and c were observed. It should be noted that all the prepared compositions $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ ($0 < x \leq 2$) were formed, however, none of these phases were pure. The samples had to be heated below the melting point of AgVO_3 ($T = 476^\circ\text{C}$) to avoid the segregation of liquid and solid phases. This has made the reaction kinetics between the starting materials slow. All the samples contained impurity phases that could not be identified. This has made the Rietveld refinements and the phase quantification difficult. Therefore, in the next sections the focus will be on single-crystal structure analyses.

3.1.2 Single-crystal X-ray diffraction

The structures of $\text{Ag}_{0.15}\text{Na}_{1.85}\text{Mn}_3(\text{VO}_4)_3$ and $\text{Ag}_{1.38}\text{Na}_{0.62}\text{Mn}_3(\text{VO}_4)_3$ were solved in the centrosymmetric space group $C2/c$. The program SUPERFLIP was used to

determine most of the atomic positions [23]. The remaining oxygen atoms were localized using difference-Fourier synthesis. It should be also noted that large residues close to the Na1 and Na2 atomic positions were observed which correspond to silver atoms. Therefore, a Na/Ag disorder in both sites was introduced and restrictions were applied ($\text{Na}_{\text{Occ.}} + \text{Ag}_{\text{Occ.}} = 1$, $\text{Na}_{\text{Position}} = \text{Ag}_{\text{Position}}$ and $\text{Na}_{\text{ADP}} = \text{Ag}_{\text{ADP}}$). After refining the anisotropic displacement parameters (ADPs) and the extinction parameter, the residual factors converged to the values listed in Table 1. The refined atomic positions and ADPs are given in Tables 3 and S1 (Supporting Information), respectively. One may notice slightly large ADPs for the sodium and silver atoms. This is most likely due to the high mobility of these atoms. The refinement of the occupancy of the V and Mn atoms did not show any deviation from the standard values. One should mention that in the Mn2 site, there is a disorder of Mn^{2+} and Mn^{3+} cations and it would be possible to refine the structure using a lower symmetry to order these atoms. Several alluaudite compounds crystallize with the space group $P2_1/c$. However, our extinction conditions are not compatible with such a space group.

3.2 Crystal structure

The $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ compounds crystallize with the well-known alluaudite-type structure as do $\text{Ag}_2\text{Mn}_3(\text{VO}_4)_3$ and $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_2\text{Fe}(\text{VO}_4)_3$ [20, 21]. In this structure the octahedra share edges end form MnO_4 infinite chains along the $[10\bar{1}]$ direction (Fig. 1b). The VO_4 tetrahedra interconnect the MnO_4 chains to form a three dimensional $[\text{Mn}_3(\text{VO}_4)_3]^{2-}$ framework with channels along the c axis, in which are located the Ag/Na atoms (Fig. 1a). The interatomic distances, angles and bond valence sums (BVSs) [24, 25] are listed in Table 4.

In $\text{Ag}_{0.15}\text{Na}_{1.85}\text{Mn}_3(\text{VO}_4)_3$, the manganese atoms are located in distorted octahedra with Mn–O distances ranging from 2.168 to 2.220 $\text{\AA}$ and from 2.018 to 2.266 $\text{\AA}$ with the average distances of 2.191 and 2.092 $\text{\AA}$ for Mn1–O and Mn2–O, respectively. These distances are similar to those of Mn1–O in $\text{Na}_2\text{Mn}_{3/2}\text{Fe}_{3/2}(\text{PO}_4)_3$, and Mn2–O in

Table 2: Crystallographic data for $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ powder samples.

Compositions (x)	a ($\text{\AA}$)	b ($\text{\AA}$)	c ($\text{\AA}$)	β (deg)	V ($\text{\AA}^3$)
2	11.9155(2)	13.0232(4)	6.8539(2)	111.668(2)	988.42(5)
1.9	11.8673(5)	13.1430(6)	6.8203(3)	111.622(4)	988.93(8)
3/2	11.8825(4)	13.1361(6)	6.8108(3)	111.463(3)	989.36(9)
1/2	11.9013(5)	13.1833(4)	6.8120(3)	111.407(3)	995.05(10)
0	11.9062(4)	13.2079(4)	6.8103(2)	111.408(2)	997.07(8)

Table 3: Atom positions and equivalent ADP ($\text{\AA}^2$) for $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ ($x=0.62$ and 1.85).

Atom	Wyck.	Symm.	Occup.	x	y	z	U_{eq} ($\text{\AA}^2$)
$x=0.62$							
Ag1/Na1	4b	$\bar{1}$	0.680(4)/0.320(4)	1/2	0	0	0.0334(4)
Ag2/Na2	4e	2	0.696(4)/0.304(4)	1/2	0.49086(7)	1/4	0.0364(4)
Mn1	4e	2	1	0	0.26799(8)	1/4	0.0183(4)
Mn2	8f	1	1	0.21082(7)	0.15953(7)	0.12476(10)	0.0234(3)
V1	4e	2	1	0	0.29216(10)	3/4	0.0201(4)
V2	8f	1	1	0.72913(7)	0.38892(8)	0.12244(11)	0.0205(3)
O1	8f	1	1	0.6582(3)	0.5043(3)	0.1016(6)	0.0255(14)
O2	8f	1	1	0.1616(3)	0.1732(3)	0.3825(5)	0.0239(11)
O3	8f	1	1	0.7142(3)	0.3194(3)	0.3260(5)	0.0313(13)
O4	8f	1	1	0.8786(3)	0.4045(3)	0.1780(6)	0.0382(15)
O5	8f	1	1	0.0391(3)	0.2196(3)	0.9787(4)	0.0229(11)
O6	8f	1	1	0.1110(4)	0.3744(3)	0.7526(5)	0.0410(15)
$x=1.85$							
Ag1/Na1	4b	$\bar{1}$	0.110(3)/0.890(3)	1/2	0	0	0.0253(7)
Ag2/Na2	4e	2	0.042(3)/0.958(3)	1/2	0.49775(20)	1/4	0.0380(10)
Mn1	4e	2	1	0	0.27057(6)	1/4	0.0126(3)
Mn2	8f	1	1	0.20985(5)	0.16003(5)	0.12220(8)	0.0156(2)
V1	4e	2	1	0	0.29122(7)	3/4	0.0170(3)
V2	8f	1	1	0.72844(5)	0.38944(5)	0.11993(9)	0.0122(2)
O1	8f	1	1	0.6570(2)	0.50409(19)	0.0968(4)	0.0178(9)
O2	8f	1	1	0.1604(2)	0.1719(2)	0.3783(4)	0.0181(9)
O3	8f	1	1	0.7137(2)	0.3202(2)	0.3260(4)	0.0204(9)
O4	8f	1	1	0.8775(2)	0.4037(2)	0.1752(4)	0.0214(9)
O5	8f	1	1	0.0392(2)	0.2203(2)	0.9811(4)	0.0161(8)
O6	8f	1	1	0.1118(3)	0.3732(2)	0.7577(4)	0.0356(12)

Fig. 1: Projection view along [001] of the structure of $\text{Ag}_{0.15}\text{Na}_{1.85}\text{Mn}_3(\text{VO}_4)_3$ (a), view along [101] of the MnO_4 infinite chains of edge-sharing octahedra (b), and coordination spheres of the Na1/Ag1 (c) and Na2/Ag2 cations (d).

$\text{Ag}_{1.5}\text{Mn}_3(\text{AsO}_4)_3$ [26, 27] with average distances at 2.186 $\text{\AA}$ [26] and 2.096 $\text{\AA}$ [27], respectively. The BVS values of 2.035 and 2.685 are in agreement with the values of +2 and +2.5 for the divalent and mixed-valent Mn1 and Mn2 atoms. The VO_4 tetrahedra are regular. The V–O distances range from 1.696 to 1.742 $\text{\AA}$ and from 1.680 to 1.744 $\text{\AA}$ with the average values of 1.719 and 1.718 $\text{\AA}$ for V1 and V2, respectively (Table 4). The BVS of 5.030 and 5.052 are in very good agreement with the value of +5 expected for pentavalent vanadium atoms. The sodium and silver atoms Na1/Ag1 and Na2/Ag2 are eight coordinated to

oxygen atoms (Fig. 1c, d). The BVS values of 1.026/1.140 and 0.873/0.970 for Na1/Ag1 and Na2/Ag2, respectively, indicate that the Na2 and Ag2 atoms are under-bonded even after increasing the coordination sphere to 3.2 $\text{\AA}$.

3.2.1 Evaluation of the structural similarity of $\text{Ag}_2\text{Mn}_3(\text{VO}_4)_3$ and $\text{Ag}_{0.15}\text{Na}_{1.85}\text{Mn}_3(\text{VO}_4)_3$

It is very surprising to see that replacing silver ($R_{\text{ionic}} = 1.28 \text{ \AA}$) by sodium ($R_{\text{ionic}} = 1.18 \text{ \AA}$) atoms does not

Table 4: Interatomic distances (in Å), BVSS^a and angles (deg) for Ag_{2-x}Na_xMn₃(VO₄)₃ (x=0.62 and 1.85).

Compounds	Distances and angles		
	Ag ₂ Mn ₃ (VO ₄) ₃	Ag _{1.38} Na _{0.62} Mn ₃ (VO ₄) ₃	Ag _{0.15} Na _{1.85} Mn ₃ (VO ₄) ₃
Ag1/Na1–O6 (×2)	2.462(3)	2.413(4)	2.430(3)
Ag1/Na1–O4 (×2)	2.544(2)	2.495(4)	2.501(3)
Ag1/Na1–O4 (×2)	2.551(3)	2.573(5)	2.540(3)
Ag1/Na1–O6 (×2)	2.992(4)	3.033(5)	2.986(4)
<Ag1/Na1–O>	<2.637>	<2.629>	<2.514>
Ag1/Na1 ^a	1.058 [8]	1.128/1.015 [8]	1.140/1.026 [8]
Ag2/Na2–O1 (×2)	2.437(3)	2.462(3)	2.413(2)
Ag2/Na2–O1 (×2)	2.459(4)	2.496(5)	2.457(3)
Ag2/Na2–O2 (×2)	2.990(3)	3.015(4)	2.897(3)
Ag2/Na2–O5 (×2)	3.196(3)	3.137(4)	3.218(4)
<Ag2/Na2–O>	<2.771>	<2.778>	<2.746>
Ag2/Na2 ^a	0.920 [8]	0.860/0.774 [8]	0.970/0.873 [8]
Mn1–O5 (×2)	2.137(3)	2.193(4)	2.161(3)
Mn1–O2 (×2)	2.207(3)	2.209(3)	2.201(3)
Mn1–O4 (×2)	2.210(3)	2.256(4)	2.210(3)
<Mn1–O>	<2.184>	<2.219>	<2.191>
Mn1 ^a	2.072 [6]	1.885 [6]	2.035 [6]
Mn2–O6	2.017(4)	2.048(5)	2.018(3)
Mn2–O2	2.035(3)	2.086(4)	2.049(3)
Mn2–O5	2.041(3)	2.094(3)	2.055(2)
Mn2–O3	2.054(3)	2.097(4)	2.058(3)
Mn2–O1	2.126(3)	2.130(4)	2.129(3)
Mn2–O3	2.273(3)	2.268(4)	2.266(3)
<Mn2–O>	<2.091>	<2.121>	<2.096>
Mn2 ^a	2.620 [6]	2.495 [6]	2.685 [6]
V1–O6 (×2)	1.708(4)	1.721(5)	1.696(4)
V1–O5 (×2)	1.743(2)	1.752(3)	1.742(3)
<V1–O>	<1.726>	<1.737>	<1.719>
V1 ^a	4.938 [4]	4.790 [4]	5.030 [4]
V2–O4	1.677(3)	1.716(4)	1.680(3)
V2–O1	1.728(3)	1.726(4)	1.707(3)
V2–O3	1.737(3)	1.743(4)	1.739(3)
V2–O2	1.745(2)	1.750(3)	1.744(2)
<V2–O>	<1.722>	<1.734>	<1.718>
V2 ^a	4.996 [4]	4.830 [4]	5.052 [4]
O6–V1–O6	103.31(17)	102.0(2)	101.23(17)
O5–V1–O6 (×2)	108.35(14)	107.32(18)	108.10(14)
O5–V1–O6 (×2)	110.42(12)	112.91(15)	111.59(12)
O5–V1–O5	115.33(13)	113.83(19)	115.35(13)
<O–V1–O>	<109.35>	<109.02>	<109.07>
O1–V2–O2	107.56(12)	107.03(16)	106.22(12)
O3–V2–O4	106.30(13)	107.70(18)	106.91(13)
O1–V2–O3	110.35(16)	109.3(2)	109.83(15)
O2–V2–O4	109.06(14)	110.2(2)	110.16(14)
O1–V2–O4	111.63(15)	111.3(2)	111.76(13)
O2–V2–O3	111.99(13)	111.35(18)	112.03(13)
<O–V2–O>	<109.48>	<109.48>	<109.49>

Average values are given in <>. Coordination numbers of atoms are given in []. ^aBond valence sum, B.V. = exp{(r₀–r)/b} with the following parameters: b = 0.37, r₀ (Ag^I–O) = 1.842, r₀ (Na^I–O) = 1.803, r₀ (Mn^{II}–O) = 1.790, r₀ (Mn^{III}–O) = 1.76 and r₀ (V^V–O) = 1.803 Å [24, 25].

affect at all the average Na2/Ag2–O distances which remain almost identical (Table 4). However, the average Na1/Ag1–O distances decrease significantly from 2.637 in Ag₂Mn₃(VO₄)₃ to 2.514 Å in Ag_{0.15}Na_{1.85}Mn₃(VO₄)₃. Using the program COMPSTRU, we investigated and quantified the difference between the structures of Ag₂Mn₃(VO₄)₃

Table 5: Atom pairings and their distances for comparison of $\text{Ag}_2\text{Mn}_3(\text{VO}_4)_3$ and $\text{Ag}_{0.15}\text{Na}_{1.85}\text{Mn}_3(\text{VO}_4)_3$ structures.^a

	WP	Atoms		Atomic displacements			
		(x=0)	(x=1.85)	u_x	u_y	u_z	u
4b	(0, 1/2, 0)	Ag1	Ag1/Na1	0.0000	0.0000	0.0000	0.0000
4e	(0, y, 1/4)	Ag2	Ag2/Na2	0.0000	0.0051	0.0000	0.0677
4e	(0, y, 1/4)	Mn1	Mn1	0.0000	0.0011	0.0000	0.0147
8f	(x, y, z)	Mn2	Mn2	0.0019	-0.0004	0.0034	0.0266
4e	(0, y, 1/4)	V1	V1	0.0000	-0.0016	0.0000	0.0206
8f	(x, y, z)	V2	V2	0.0004	0.0008	0.0008	0.0126
8f	(x, y, z)	O1	O1	-0.0013	-0.0009	-0.0019	0.0199
8f	(x, y, z)	O2	O2	-0.0017	-0.0013	0.0005	0.0276
8f	(x, y, z)	O3	O3	-0.0001	0.0008	0.0003	0.0109
8f	(x, y, z)	O4	O4	0.0010	0.0029	0.0027	0.0418
8f	(x, y, z)	O5	O5	0.0004	-0.0019	-0.0003	0.0258
8f	(x, y, z)	O6	O6	-0.0028	0.0002	-0.0028	0.0319

^a u_x , u_y and u_z are given in relative units. |u| is the absolute distance given in Å.

Table 6: Atom pairings and their distances for comparison of $\text{Ag}_2\text{Mn}_3(\text{VO}_4)_3$ and $\text{Ag}_{1.38}\text{Na}_{0.62}\text{Mn}_3(\text{VO}_4)_3$ structures.^a

	WP	Atoms		Atomic displacements			
		(x=0)	(x=0.62)	u_x	u_y	u_z	u
4b	(0, 1/2, 0)	Ag1	Ag1/Na1	0.0000	0.0000	0.0000	0.0000
4e	(0, y, 1/4)	Ag2	Ag2/Na2	0.0000	-0.0018	0.0000	0.0232
4e	(0, y, 1/4)	Mn1	Mn1	0.0000	-0.0015	0.0000	0.0194
8f	(x, y, z)	Mn2	Mn2	0.0029	-0.0009	0.0060	0.0443
4e	(0, y, 1/4)	V1	V1	0.0000	-0.0006	0.0000	0.0082
8f	(x, y, z)	V2	V2	0.0011	0.0003	0.0033	0.0220
8f	(x, y, z)	O1	O1	-0.0001	-0.0007	0.0029	0.0221
8f	(x, y, z)	O2	O2	-0.0005	0.0000	0.0047	0.0346
8f	(x, y, z)	O3	O3	0.0004	0.0000	0.0003	0.0044
8f	(x, y, z)	O4	O4	0.0021	0.0037	0.0055	0.0607
8f	(x, y, z)	O5	O5	0.0003	-0.0026	-0.0027	0.0397
8f	(x, y, z)	O6	O6	-0.0036	0.0014	-0.0079	0.0583

^a u_x , u_y and u_z are given in relative units. |u| is the absolute distance given in Å.

and $\text{Ag}_{0.15}\text{Na}_{1.85}\text{Mn}_3(\text{VO}_4)_3$ and our results are presented in Table 5. The inspection of Table 5 shows that the highest value for |u| was observed for the atom Ag2/Na2. The degree of lattice distortion (S) represents the spontaneous strain (sum of the squared eigenvalues of the strain tensor divided by 3). For the given two structures, the degree of lattice distortion (S) is 0.0030. The maximum distance (d_{max}) shows the maximal displacement between the atomic positions of the paired atoms. The maximum distance (d_{max}) in this case is 0.0677 Å, while the arithmetic mean (d_{av}) is 0.0249 Å. The measure of similarity (Δ) is a function of the differences in atomic positions (weighted by the multiplicities of the sites) and the ratios of the corresponding lattice parameters of the structures. The measure of similarity (Δ) calculated for this case is 0.006 [28–31].

3.2.2 Evaluation of the structure similarity of $\text{Ag}_2\text{Mn}_3(\text{VO}_4)_3$ and $\text{Ag}_{1.38}\text{Na}_{0.62}\text{Mn}_3(\text{VO}_4)_3$

The interatomic distances given in Table 4 and the similarity parameters (S)=0.0070, (d_{max})=0.0607 Å, (d_{av})=0.0312 Å and (Δ)=0.031, show that the two structures are essentially coincident. Table 6 shows that the highest values for |u| was observed for the atoms O4 and O6.

4 Conclusion

Compounds with the compositions $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ ($0 \leq x \leq 2$) were synthesized by a solid state reaction route and the crystal structures of $\text{Ag}_{1.38}\text{Na}_{0.62}\text{Mn}_3(\text{VO}_4)_3$ ($x=0.62$) and $\text{Ag}_{0.15}\text{Na}_{1.85}\text{Mn}_3(\text{VO}_4)_3$ ($x=1.85$) have been

solved using single-crystal X-ray diffraction. Both compounds crystallize with the well-known alluaudite-type structure with Ag/Na statistical disorder over a 4b and a 4e atomic position. Although, a pure $\text{Na}_2\text{Mn}_3(\text{VO}_4)_3$ phase could not be obtained for further electrochemical studies, this structural study based on single-crystal X-ray diffraction data confirms the existence of a full solid solution $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ ($0 \leq x \leq 1.85$) and opens new perspectives for the discovery of new class of materials for sodium ion battery and solid electrolyte applications.

5 Supporting information

The shapes of the single crystals used for the data collection (Fig. S1) and the anisotropic displacement parameters ($\text{\AA}^2$) for $\text{Ag}_{2-x}\text{Na}_x\text{Mn}_3(\text{VO}_4)_3$ ($x = 0.62$ and 1.85) (Table S1) are given as supplementary material available online (DOI: 10.1515/znb-2019-0116).

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