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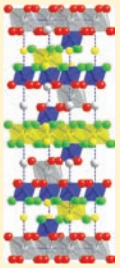
$Na_{1.5}Ag_{1.5}MO_3F_3$ (M = Mo, W): An Ordered Oxyfluoride Derivative of the $LiNbO_3$ Structure

Allyson M. Fry, Harry A. Seibel, II, Indunil N. Lokuhewa, and Patrick M. Woodward*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210-1185, United States

Supporting Information

ABSTRACT: $Na_{1.5}Ag_{1.5}MoO_3F_3$ and $Na_{1.5}Ag_{1.5}WO_3F_3$ have been synthesized by solid state reactions and structurally characterized using synchrotron X-ray and neutron powder diffraction. Unlike the vast majority of salts containing $[MO_3F_3]^{3-}$ anions (M = Mo, W) the oxyfluoride groups in $Na_{1.5}Ag_{1.5}MoO_3F_3$ and $Na_{1.5}Ag_{1.5}WO_3F_3$ are orientationally ordered, so that the Na^+ ions are coordinated by fluorine and the Ag^+ ions by oxygen. The resulting structure type, which has not previously been reported, is related to the $LiNbO_3$ structure, but the combination of Na/Ag ordering and orientational ordering of the $[MO_3F_3]^{3-}$ anions produces a supercell that doubles the *c*-axis and changes the space group symmetry from *R*3 to $R\bar{3}$. The use of hard (Na^+) and soft (Ag^+) cations to direct the orientational ordering of polar oxyfluoride building units provides a new approach to the design of polar materials.



INTRODUCTION

Compounds that crystallize with polar structures are an important class of functional materials that include ferroelectrics (e.g., $BaTiO_3$), piezoelectrics (e.g., $PbZr_{1-x}Ti_xO_3$), multiferroics (e.g., $BiFeO_3$), and many important nonlinear optical materials (e.g., $LiNbO_3$, $KTiOPO_4$).[1,2] From a bottom-up materials design perspective it is appealing to start with polar building units and rationally assemble those units so that the dipole moments add constructively. Unfortunately, in many instances the polar building units fail to orientationally order, frustrating attempts to prepare new polar materials. The ability to control the orientations of polar building units remains an elusive challenge in crystal design and engineering.

Salts containing $[MoO_3F_3]^{3-}$ and $[WO_3F_3]^{3-}$ anions are potentially an important source of polar materials. Not only is the $[MoO_3F_3]^{3-}$ anion highly polar, with an approximate dipole moment of ~6 D,[3] there is a large family of such compounds, including $A_2M'MO_3F_3$ and $A_3MO_3F_3$ (A = K, Rb, Cs, Tl; M′ = K, Rb ; M = Mo, W).[4−8] Despite the fact that these compounds have been studied for decades, dating back to the work of Pauling,[9] there are very few examples where the $[MO_3F_3]^{3-}$ units are ordered. Maggard et al. were the first to achieve ordering of $[MoO_3F_3]^{3-}$ polyhedra in the complex salt $(Ag_3MoO_3F_3)(Ag_3MoO_4)Cl$.[3] This behavior was attributed to dipole−dipole interactions between $[MoO_3F_3]^{3-}$ and distorted $[MoO_4]^{2-}$ groups. Later Brink et al. showed that the $[MoO_3F_3]^{3-}$ units are ordered in $Na_3MoO_3F_3$.[10,11] The rationale given for polar ordering in $Na_3MoO_3F_3$, when it is absent in most perovskite type $A_2M'MO_3F_3$ compounds, was based the relative sizes of the A and M′ cations. Cation size is also thought to be at least partially responsible for ordering of polar $[NbOF_5]^{2-}$ units in $KNaNbOF_5$ and $CsNaNbOF_5$.[12]

A relatively unexplored strategy for ordering polar building units is to use differences in bonding preferences of the cations surrounding the oxyfluoride anions to direct their orientation. In this contribution we show that by using a combination of Na^+ and Ag^+ cations in a 1:1 ratio we can direct orientational ordering of $[MoO_3F_3]^{3-}$ and $[WO_3F_3]^{3-}$ units. The resulting rhombohedral structure represents the first example of an anion-ordered derivative of the $LiNbO_3$ structure.

EXPERIMENTAL SECTION

$Na_{1.5}Ag_{1.5}MO_3F_3$ (M = Mo, W) samples were synthesized through solid-state reaction of stoichiometric amounts of NaF (Acros), AgF (Acros), and WO_3/MoO_3 (Alfa Aesar). Due to the hygroscopic nature of AgF, the reactants were ground with an agate mortar and pestle in an argon filled glovebox. Before removal from the glovebox the samples were placed in silver tubes that were crimped to retain the argon atmosphere of the glovebox. Finally the tubes were sealed using a H_2/O_2 torch, placed in a box furnace, and heated to 425 °C for 35 h followed by three heatings to 550 °C for 72 h with intermediate grindings in the glovebox. Care was taken to avoid exposure to moisture until the reaction was complete in order to prevent unreacted AgF from picking up water.

X-ray powder diffraction (XRPD) data were collected on a Bruker D8 powder diffractometer (40 kV, 50 mA, sealed Cu X-ray tube) equipped with an incident beam Ge 111 monochromator and Lynx eye position sensitive detector. Time-of-flight neutron powder diffraction (NPD) data were collected for $Na_{1.5}Ag_{1.5}MoO_3F_3$ on the high resolution powder diffractometer (HRPD) at the ISIS facility of the Rutherford Appleton Laboratory. Synchrotron X-ray diffraction (λ = 0.412395 Å) was collected on beamline 11-BM at the Advanced Photon Source, APS, at Argonne National Laboratory. Structural refinements of XRPD and synchrotron data were carried out using TOPAS Academic software package using the Rietveld method.[13] Rietveld refinement of NPD was performed via the GSAS software package.[14,15]

RESULTS

Laboratory X-ray powder diffraction data were collected on a sample of $Na_{1.5}Ag_{1.5}MoO_3F_3$. Using the autoindexing program TREOR,[16] as implemented in the CRYSFIRE suite,[17] peaks were indexed to a hexagonal cell with dimensions $a \approx 5.75$ Å

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and $c \approx 28.5$ Å, with systematic absences consistent with rhombohedral centering. The unit cell dimensions suggest the structure of $Na_{1.5}Ag_{1.5}MoO_3F_3$ is related in some way to that of $Na_3MoO_3F_3$ (space group $R3$ with $a \approx 5.75$ Å and $c \approx 14.2$ Å).[10] As described by Brink et al. the structure of $Na_3MoO_3F_3$ can be derived from the ordered double perovskite structure by $a^-a^-a^-$ rotations of the octahedra and parallel displacements of the molybdenum ions, which are driven by anion ordering (i.e., orientational ordering of the $[MoO_3F_3]^{3-}$ groups).

Building on the similarities to $Na_3MoO_3F_3$, the program ISODISPLACE was used to generate a structure that could serve as a starting model for refinements.[18] The model that was generated possessed $R\bar{3}$ (148) space group symmetry and lattice parameters $a \approx 5.75$ Å and $c \approx 28.5$ Å. It was derived from the ordered double perovskite structure by introducing (1) $a^-a^-a^-$ rotations of the octahedra, and (2) a more complex pattern of anion ordering than seen in $Na_3MoO_3F_3$. The second feature was necessary to explain the doubling of the c-axis in $Na_{1.5}Ag_{1.5}MoO_3F_3$ (28.5 Å) with respect to $Na_3MoO_3F_3$ ($c \approx 14.2$ Å). The ordering of Na and Ag was determined from refinements of site occupancies. Using this approach the refinement converged to an acceptable fit, R_{wp}= 0.044.

To test the uniqueness of this result, refinements were also carried out with a model where the symmetry was lowered to $R3$ (146). Despite an increase in the number of parameters the fit was not as good as that obtained with $R\bar{3}$. A search of the International Crystal Structure Database (ICSD) of Fachinformationszentrum Karlsruhe, Germany showed that Ba_2NiTeO_6 adopts a structure with $R\bar{3}m$ (166) symmetry and similar lattice parameters.[19] This structure was also used as a starting point for the refinements, but starting from this model it was not possible to obtain an acceptable fit to the data.

To obtain the most accurate description of the structure time-of-flight neutron diffraction data were collected on HRPD at the ISIS spallation neutron source and synchrotron X-ray diffraction data were collected on beamline 11-BM at the Advanced Photon Source. Starting with the atomic coordinates obtained from laboratory X-ray data, refinements of both synchrotron and neutron data rapidly converged. The results are given in Tables 1 and 2. The final fit of the neutron data is shown in Figure 1, while the fit to the synchrotron data is given in the Supporting Information. The crystal structure is shown in Figure 2. Synchrotron data allowed for further refinement of the cation site occupancies, which revealed that a small amount of mixing between silver and sodium occurs on the 6c sites; however, no mixing occurs on the 3a or 3b sites. The occupancies used in the neutron refinement were fixed at the values obtained from the synchrotron data set.

Table 1. Structural Refinements Obtained from TOF Neutron Data and Synchrotron Data

cmpd	$Na_{1.5}Ag_{1.5}MoO_3F_3$	$Na_{1.5}Ag_{1.5}MoO_3F_3$	$Na_{1.5}Ag_{1.5}WO_3F_3$
space group	$R\bar{3}$(148)	$R\bar{3}$(148)	$R\bar{3}$(148)
a (Å)	5.73669(9)	5.75455(1)	5.74147(2)
c (Å)	28.4715(6)	28.50391(8)	28.6379(1)
V (Å^3)	811.43(3)	817.443(4)	817.557(6)
λ (Å)	1.540596	0.412395	0.412395
data type	TOF neutron	synchrotron	synchrotron
number of reflections	424	244	243
program used for Rietveld refinement	GSAS	Topas Academic	Topas Academic
R_{wp}	0.04	13.01	8.86
χ^2	1.52	1.12	1.03

A sample of $Na_{1.5}Ag_{1.5}WO_3F_3$ was also prepared and found to be isostructural with $Na_{1.5}Ag_{1.5}MoO_3F_3$. Synchrotron data for $Na_{1.5}Ag_{1.5}WO_3F_3$ were collected and refined; the final fit of the synchrotron data is given in Figure 3. The results are also given in Tables 1 and 2. The cation site mixing seen in $Na_{1.5}Ag_{1.5}MoO_3F_3$ is not observed in the tungsten analogue. In both molybdenum and tungsten compounds bond valences (see Table 4) were used to assign oxygen and fluorine positions. The bond distances and valences unambiguously show that oxygen and fluorine order onto two crystallographic sites.

The bond lengths (Table 3) in $Na_{1.5}Ag_{1.5}MoO_3F_3$ and $Na_{1.5}Ag_{1.5}WO_3F_3$ are very similar. For both compounds the bond valence sums are quite close to the oxidation states of the individual ions (Table 4), validating the accuracy of the refinements. Comparison of the bond valence sums for $Na_{1.5}Ag_{1.5}MoO_3F_3$ obtained from neutron and synchrotron data (Table 4) shows that the structure obtained from neutron data has bond valences that are in slightly better agreement with expected values. This is most likely a result of the well-known fact that the positions of light atoms (here O and F) can be more accurately determined from neutron data. Within this context it is also interesting to note that the Mo−O and Mo−F bond distances determined from the X-ray data set are very similar to the analogous distances in $Na_{1.5}Ag_{1.5}WO_3F_3$. Presumably these distances would also be very similar if we had been able to obtain a neutron data set for $Na_{1.5}Ag_{1.5}WO_3F_3$. Thus, the overbonding of tungsten seen in Table 4 is likely an artifact of the accuracy of the synchrotron-based refinement.

The Mo−O and Mo−F bond lengths in $Na_{1.5}Ag_{1.5}MoO_3F_3$ are very similar to the W−O and W−F bond lengths in $Na_{1.5}Ag_{1.5}WO_3F_3$. In both compounds the d^0 cation has shifted much closer to the oxygen face of its octahedron. Similar Mo−O and Mo−F bond lengths have been observed in $(Ag_3MoO_3F_3)(Ag_3MoO_4)Cl$, $d_{Mo-O} = 1.755(6)$ Å and $d_{Mo-F} = 2.083(5)$ Å, as well as $Na_3MoO_3F_3$, $d_{Mo-O} = 1.765(5)$ Å and $d_{Mo-F} = 2.116(5)$ Å.[3,10] The similarities across the three compounds show a constancy of bonding within the $[MoO_3F_3]^{3-}$ polyatomic anion and reinforces the notion that these compounds are best described as salts.

■ DISCUSSION

Although the starting model for the refinements was based on an ordered perovskite structure, the final structure is actually more closely related to the $LiNbO_3$ structure. The $LiNbO_3$ and perovskite structures both exhibit the same topology of corner connected MO_6 octahedra, but they differ in the coordination environment of the larger A-site cation. In perovskite the A-site cation sits in the center of the eight MO_6 octahedra and is surrounded by 12 oxygens in a cuboctahedral environment. In $LiNbO_3$ the lithium sits in an octahedron that shares one face with a neighboring NbO_6 octahedron. Due to electrostatic repulsions the Li^+ ions undergo a large shift parallel to the c-axis away from the shared face of the octahedron, leading to Li−O distances of $d_{Li-O} = 3 \times 2.12(8)$ Å and 3×2.41 Å.[20]

In $Na_{1.5}Ag_{1.5}MO_3F_3$ (M = Mo, W) the Ag(2), Na(2), and Mo/W atoms reside on octahedral sites that are occupied by niobium ions in $LiNbO_3$. These octahedra share corners to form the framework that holds the structure together. Viewed perpendicular to the c-axis we see a repeating Ag(2)−Mo−

Table 2. Atomic Positions for $Na_{1.5}Ag_{1.5}MO_3F_3$ (M = Mo,W) Obtained from Neutron and Synchrotron Data

atom	Wyckoff position	x	y	z	occupancy	U_{iso}
$Na_{1.5}Ag_{1.5}MoO_3F_3$ neutron						
Ag(1a)	6c	0	0	0.3759(2)	0.881	0.034(1)
Na(1a)					0.119	
Na(1b)	6c	0	0	0.1389(3)	0.881	0.039(2)
Ag(1b)					0.119	
Ag(2)	3a	0	0	0	1	0.027(2)
Na(2)	3b	0	0	0.5	1	0.046(4)
Mo	6c	0	0	0.2579(1)	1	0.020(8)
O	18f	0.5848(6)	0.9580(7)	0.3815(1)	1	0.030(3)[a]
F	18f	0.5763(6)	0.9491(7)	0.8742(1)	1	0.028(3)[a]
$Na_{1.5}Ag_{1.5}MoO_3F_3$ synchrotron						
Ag(1a)	6c	0	0	0.37439(3)	0.881(1)	0.016(1)
Na(1a)					0.119(1)	
Na(1b)	6c	0	0	0.13356(3)	0.881(1)	0.016(1)
Ag(1b)					0.119(1)	
Ag(2)	3a	0	0	0	1	0.016(2)
Na(2)	3b	0	0	0.5	1	0.016(2)
Mo	6c	0	0	0.25753(3)	1	0.007(8)
O	18f	0.5885(7)	0.9494(8)	0.3821(2)	1	0.017(3)
F	18f	0.5668(6)	0.9393(6)	0.8733(1)	1	0.017(3)
$Na_{1.5}Ag_{1.5}WO_3F_3$ synchrotron						
Ag(1)	6c	0	0	0.36958(3)	1	0.021(8)
Na(1)	6c	0	0	0.1330(1)	1	0.021(8)
Ag(2)	3a	0	0	0	1	0.014(8)
Na(2)	3b	0	0	0.5	1	0.014(8)
W	6c	0	0	0.25496(1)	1	0.006(9)
O	18f	0.6227(7)	0.9217(6)	0.9474(1)	1	0.014(6)
F	18f	0.6106(5)	0.9058(5)	0.4616(1)	1	0.014(6)

[a] U_{eq} is defined as one-third of the trace of the orthogonal U_{ij} tensor; refined anisotropic displacement parameters were $U_{11} = 0.028(2)$, $U_{22} = 0.022(2)$, $U_{33} = 0.040(2)$, $U_{12} = 0.0081(2)$, $U_{13} = 0.009(1)$, $U_{23} = 0.011(1)$ for O and, $U_{11} = 0.023(2)$, $U_{22} = 0.031(2)$, $U_{33} = 0.029(1)$, $U_{12} = 0.014(2)$, $U_{13} = 0.005(2)$, $U_{23} = 0.010(2)$ for F.

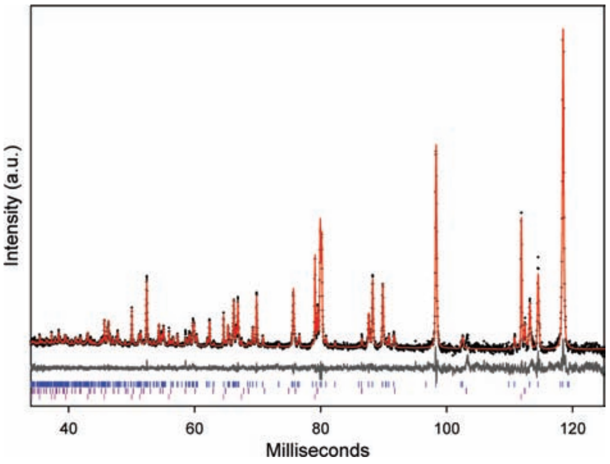

Figure 1. The refined fit (red) to high resolution TOF neutron diffraction data (black) for $Na_{1.5}Ag_{1.5}MoO_3F_3$. The top set of tick marks belongs to $Na_{1.5}Ag_{1.5}MoO_3F_3$ (95.44 wt%), the middle set of tick marks, to Ag_2MoO_4 (2.25 wt%), and the bottom set, to NaF (2.31 wt%).

Na(2)−Mo−... cation ordering sequence (Figure 2). The $[MoO_3F_3]^{3-}$ ($[WO_3F_3]^{3-}$) anions adopt an orientational ordering that results in the Ag^+ ions being exclusively coordinated by oxygen and the Na^+ ions exclusively by fluorine (if we neglect the small amount of Ag/Na disorder on the 6c sites).

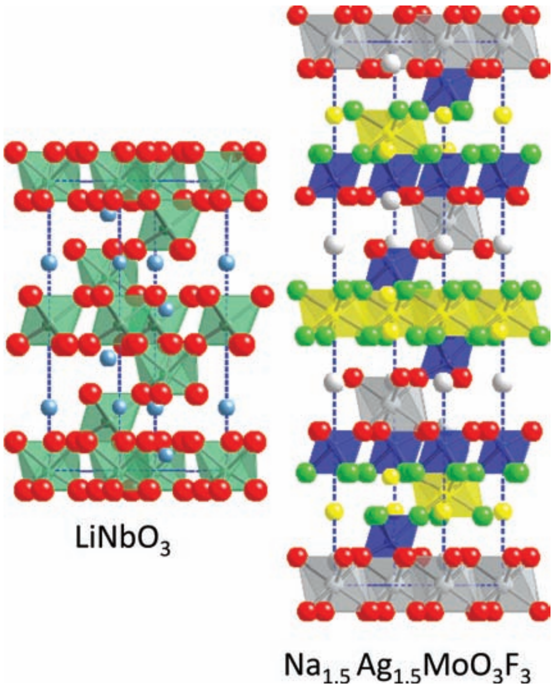

Figure 2. Crystal structures of $LiNbO_3$ and $Na_{1.5}Ag_{1.5}MoO_3F_3$ for structural comparison. Li: light blue, Na: yellow, Ag: silver, Nb: blue green, Mo: blue, O: red, F: green.

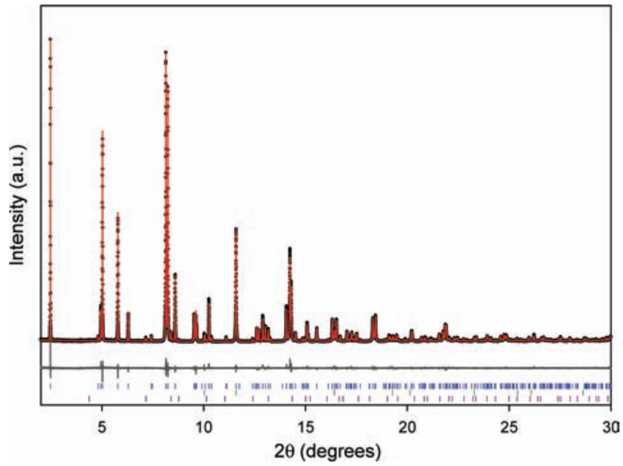

Figure 3. The refined fit (red) to synchrotron diffraction data (black) for $Na_{1.5}Ag_{1.5}WO_3F_3$. The difference curve and tick marks showing the peak positions are located at the bottom. The top set of tick marks belongs to $Na_{1.5}Ag_{1.5}WO_3F_3$ (96.31 wt%), the middle set of tick marks, to Ag (0.65 wt%), and the bottom set, to γ-Ag_2WO_4 (3.04 wt%).

Table 4. Bond Valence Sums for Neutron and Synchrotron Data for $Na_{1.5}Ag_{1.5}MO_3F_3$ (M = Mo, W)

atom	$Na_{1.5}Ag_{1.5}MoO_3F_3$ neutron	$Na_{1.5}Ag_{1.5}MoO_3F_3$ synchrotron	$Na_{1.5}Ag_{1.5}WO_3F_3$ synchrotron
Ag(1)	1.140	1.128	1.062
Na(1)	0.922	0.840	0.927
Ag(2)	1.353	1.113	1.045
Na(2)	1.063	1.003	1.112
Mo/W	5.986	6.726	6.471
F	0.963	0.962	1.002
O	2.122	2.286	2.178

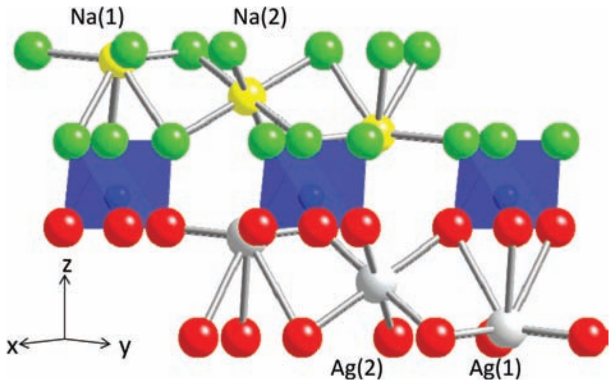

Figure 4. Cation coordination environments are shown for $Na_{1.5}Ag_{1.5}MoO_3F_3$. Silver is shown in gray, sodium in yellow, and molybdenum in blue. Oxygen and fluorine are represented by red and green spheres, respectively.

In $Na_{1.5}Ag_{1.5}MO_3F_3$ (M = Mo, W) the Ag(1) and Na(1) ions reside on the sites occupied by lithium in $LiNbO_3$. Repulsions between these ions and molybdenum lead to even greater displacements than seen in $LiNbO_3$. The distortion is so large that the Ag(1) is effectively coordinated by only three oxygens, as shown in Figure 4 and seen in the bond distances in Table 3. The Na(1) environment is slightly less distorted, but the three shortest Na−F bonds, 2.3335(7) Å, are still significantly shorter than the next three, 2.516(1) Å.

The cation ordering seen in $Na_{1.5}Ag_{1.5}MoO_3F_3$ and $Na_{1.5}Ag_{1.5}WO_3F_3$ also merits further comment. Although simultaneous ordering of both A-site and B-site cations is well established in perovskites, as discussed in a recent review,[21] it has not previously been observed in a $LiNbO_3$-type compound. These compounds are the first examples of simultaneous A- and B-site cation ordering in a $LiNbO_3$ derivative. However, it should be noted that B-site cation ordering has been previously observed in Li_2ZrTeO_6 and Li_2HfTeO_6, both of which are $LiNbO_3$ derivatives.[22]

Unfortunately, the $[MoO_3F_3]^{3-}$ anions in $Na_{1.5}Ag_{1.5}MoO_3F_3$ are oriented antiparallel from one layer to the next, so that the resulting structure is nonpolar and centrosymmetric. Despite the fact that these new compounds do not have polar structures, the observation that the $[MoO_3F_3]^{3-}$ groups align to maximize the number of Ag−O and Na−F interactions is a powerful concept that may have broad applicability. By using combinations of soft (e.g., Ag^+, Tl^+, Cd^{2+}, Pb^{2+}, etc.) and hard (alkali, alkaline-earth, and rare-earth) cations in salts of polar oxyfluoride anions (including $[TiO_{6-x}F_x]^{(8-x)-}$, $[VO_{6-x}F_x]^{(7-x)-}$, $[NbO_{6-x}F_x]^{(7-x)-}$, etc.) it should be possible to prepare additional salts with orientationally ordered anions. Some of these compounds are likely to be polar. Even in structures where the dipole moments cancel, the introduction of subtle distortions, such as octahedral tilting, could result in incomplete cancellation. This approach could open the door to new nonlinear optical, ferroelectric, and/or piezoelectric materials.

■ CONCLUSIONS

Two new oxyfluorides, $Na_{1.5}Ag_{1.5}MO_3F_3$ (M = Mo, W), have been prepared in sealed tube reactions and structurally characterized using high resolution neutron and synchrotron powder diffraction data. Their structures can be described as cation and anion ordered derivatives of the $LiNbO_3$ structure.

Table 3. Bond Lengths for Neutron and Synchrotron Data for $Na_{1.5}Ag_{1.5}MO_3F_3$ (M = Mo,W)

bond	mult.	$Na_{1.5}Ag_{1.5}MoO_3F_3$ neutron	$Na_{1.5}Ag_{1.5}MoO_3F_3$ synchrotron	$Na_{1.5}Ag_{1.5}WO_3F_3$ synchrotron
Ag(1)−O	3 ×	2.2766(3)	2.247(4)	2.2962(4)
	3 ×	3.024(6)	2.994(4)	2.992(3)
Ag(1)−F	3 ×	3.097(7)	3.181(4)	3.320(3)
Na(1)−F	3 ×	2.3291(3)	2.346(4)	2.315(3)
	3 ×	2.476(7)	2.549(4)	2.550(4)
Na(1)−O	3 ×	3.243(8)	3.152(4)	3.035(5)
Ag(2)−O	6 ×	2.3930(3)	2.454(4)	2.489(4)
Na(2)−F	6 ×	2.31744(4)	2.338(4)	2.301(3)
Mo/W−O	3 ×	1.7506(3)	1.735(3)	1.736(4)
Mo/W−F	3 ×	2.090(4)	2.064(3)	2.067(3)

The presence of hard (Na^+) and soft (Ag^+) cations drives orientational ordering of the $[MO_3F_3]^{3-}$ groups so that Na^+ ions are coordinated exclusively by fluorine and Ag^+ ions exclusively by oxygen. The use of hard/soft bonding interactions to control ordering of polyatomic oxyfluoride anions offers a new strategy to the design and preparation of polar materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional synchrotron data on $Na_{1.5}Ag_{1.5}MoO_3F_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

woodward@chemistry.ohio-state.edu

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