

## BRIEF COMMUNICATION

**Sr<sub>3</sub>MO<sub>4</sub>F (M = Al, Ga)—A New Family of Ordered Oxyfluorides**

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**Sr<sub>3</sub>MO<sub>4</sub>F has been synthesized for M = Al and Ga and shown by Rietveld refinement of neutron and synchrotron X-ray powder diffraction data to adopt a layered structure in which the oxygen and fluorine are ordered and located in different layers.** © 1999

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## INTRODUCTION

Oxyhalides and in particular oxyfluorides have recently become the renewed focus of exploratory synthesis in the search for new compounds with intriguing properties. Edwards *et al.* (1) synthesized superconducting Sr<sub>2</sub>CuO<sub>2</sub>F<sub>2+δ</sub> where the fluorine ions show a site preference for the apical sites within the K<sub>2</sub>NiF<sub>4</sub>-type structure. Due to the similar sizes of oxygen and fluorine ions many oxyfluoride structures exhibit random anion site disorder. The number of fluoride oxides with ordered fluorine and oxygen ions is rather small. They mainly have fluorite-related structures, such as ScOF (2) or ThOF<sub>2</sub> (3), or are members of the pyrochlore family, e.g., CdNdTi<sub>2</sub>O<sub>6</sub>F (4). Recently, Needs and Weller (5) have been able to prepare Ba<sub>2</sub>InO<sub>3</sub>F, where oxygen/fluorine ordering leads to a new superstructure within the K<sub>2</sub>NiF<sub>4</sub> structure type in which layers of oxide and fluoride ions are separated by (InO<sub>2</sub>) layers. Furthermore, Needs and Weller (6) also characterized Ba<sub>3</sub>In<sub>2</sub>O<sub>5</sub>F<sub>2</sub> which shows fluorine–oxygen ordering in a Ruddlesden–Popper type phase. We report here the synthesis and structural characterization of a new family of ordered oxyfluorides, Sr<sub>3</sub>MO<sub>4</sub>F (M = Al, Ga). They crystallize in a layered structure in which layers made of isolated MO<sub>4</sub> tetrahedra that contain Sr as an intercalate are separated by Sr<sub>2</sub>F layers.

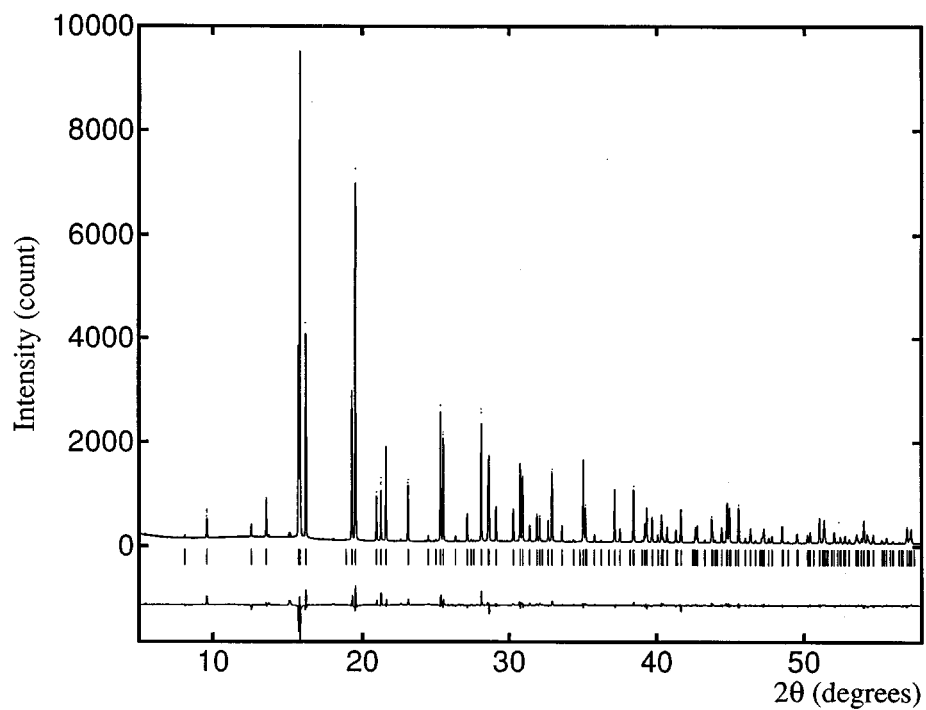
## EXPERIMENTAL

The samples were prepared by heating the appropriate amounts of Sr(CO)<sub>3</sub>, SrF<sub>2</sub>, and Ga<sub>2</sub>O<sub>3</sub> or Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O

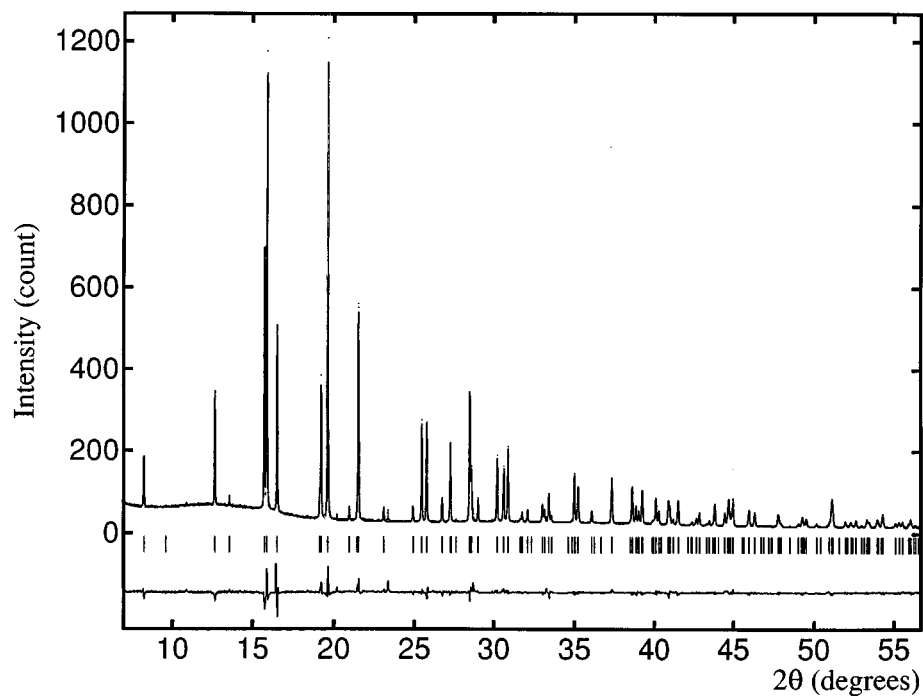
in air. The Ga compound formed after 12 h at 1100°C. The Al compound formed after being heated at 700, 800, and 900°C for 24 h each and then reground before being annealed for 72 h at 1050°C. The synchrotron X-ray diffraction patterns were measured with the high-resolution diffractometer X7A at the National Synchrotron Light Source at Brookhaven National Laboratory using a monochromatic wavelength of 0.80435 Å when measuring the Ga compound and 0.80079 Å when measuring the Al compound. The sample was in a 0.3 mm capillary and rotated during the measurement to minimize preferred orientation effects that had been noticed in an earlier run in flat-plate geometry. After successfully indexing the diffraction pattern of Sr<sub>3</sub>GaO<sub>4</sub>F in the tetragonal *I4/mcm* space group with *a* = 6.78147(5) Å and *c* = 11.3692(1) Å a search of the JCPDS database provided the similar sized unit cell of Sr<sub>2</sub>GdGaO<sub>5</sub> (7) as a starting model. Placing fluorine at the origin, a satisfactory fit to the data was achieved by the model given in Table 1.

Valence sum calculations, the results of which are listed in Table 2, indicate that the choice of positioning fluorine in the origin was correct. The ordering of the anions can also be inferred from the different Madelung site potentials of the sites. Fluorine at the origin has a site potential near 10 V, whereas the oxygen site has one close to 22 V. Both are typical values for the respective anion. The Rietveld refinement plots of the synchrotron X-ray diffraction pattern in Fig. 1 shows the fit to this model. Note that the diffuse scattering is due to the capillary and not to any indication of disorder within the structure.

The neutron powder diffraction data of Sr<sub>3</sub>GaO<sub>4</sub>F were collected at the high-resolution powder diffraction beamline at the Australian Nuclear Science and Technology Organization's research reactor at Lucas Heights (9). The wavelength used was 1.4932 Å. The sample was held in a vanadium container and rotated around its vertical axis. The results of the Rietveld refinement against the neutron



Sr<sub>3</sub>GaO<sub>4</sub>F 0.8044 Å synchrotron x-ray diffraction



Sr<sub>3</sub>AlO<sub>4</sub>F 0.8008 Å synchrotron x-ray diffraction

**FIG. 1.** Rietveld refinement plots of the synchrotron X-ray data of Sr<sub>3</sub>AlO<sub>4</sub>F (top) and Sr<sub>3</sub>GaO<sub>4</sub>F (bottom). The tick marks indicate the position of the Bragg reflections, the bottom curve is the difference between the refined model and the observed intensities.

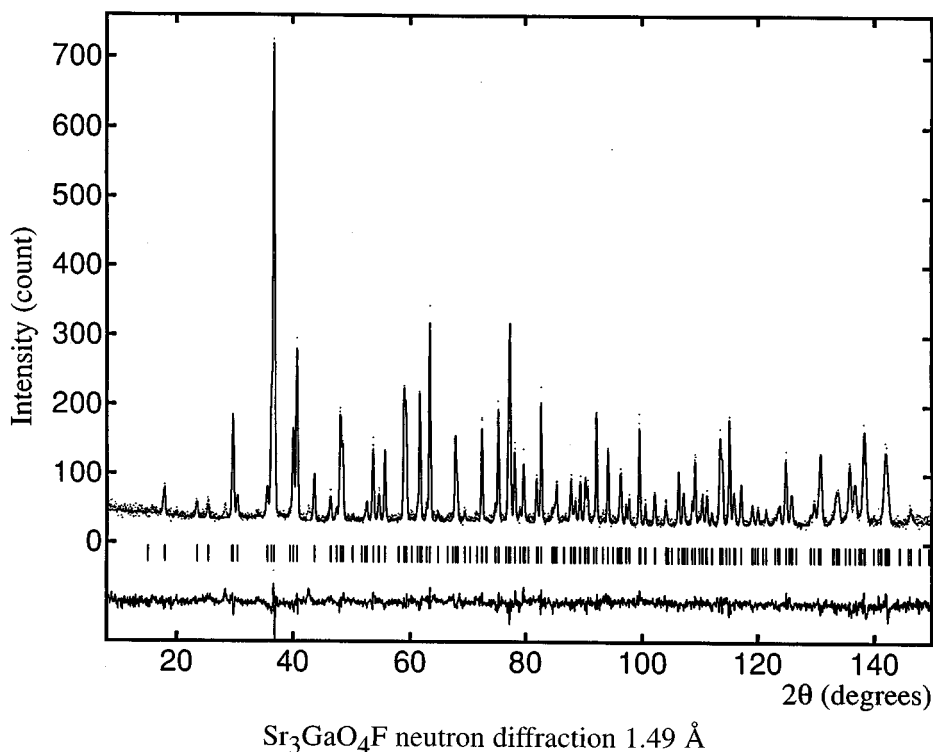


FIG. 2. Rietveld refinement of  $\text{Sr}_3\text{GaO}_4\text{F}$  using neutron powder diffraction.

TABLE 1  
Structural Parameters of  $\text{Sr}_3\text{GaO}_4\text{F}$  and  $\text{Sr}_3\text{AlO}_4\text{F}$  Obtained from Rietveld Analysis of X-Ray and Neutron Powder Diffraction Patterns

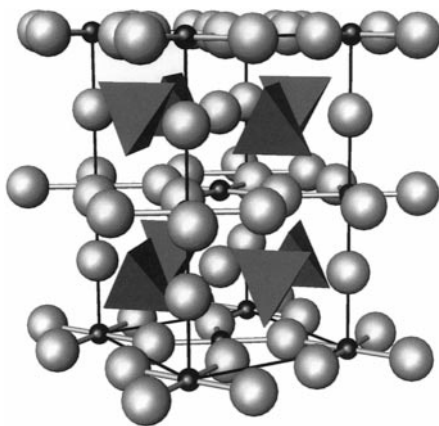
Atom	Site symmetry	x	y	z	$B_{\text{iso}}$
$\text{Sr}_3\text{GaO}_4\text{F}$ neutron					
Sr(1)	422	0	0	1/4	1.11(5)
Sr(2)	$m.2m$	0.1683	0.6683(2)	0.0	0.66(3)
Ga	$-4m2$	0	1/2	1/4	0.54(5)
F	$4/m$	0	0	0	1.29(7)
O	$m$	0.1463(2)	0.6463(2)	0.6448(2)	0.93(3)
$\text{Sr}_3\text{GaO}_4\text{F}$ X-ray					
Sr(1)	422	0	0	1/4	1.09(3)
Sr(2)	$m.2m$	0.1674(1)	0.6674(1)	0.0	0.49(2)
Ga	$-4m2$	0	1/2	1/4	0.34(3)
F	$4/m$	0	0	0	0.1(1)
O	$m$	0.1458(4)	0.6458(4)	0.6450(3)	0.09(8)
$\text{Sr}_3\text{AlO}_4\text{F}$ X-ray					
Sr(1)	422	0	0	1/4	1.11(5)
Sr(2)	$m.2m$	0.1696(1)	0.6696(1)	0.0	0.77(2)
Ga	$-4m2$	0	1/2	1/4	0.43(7)
F	$4/m$	0	0	0	0.6(2)
O	$m$	0.1418(5)	0.6418(5)	0.6496(3)	0.21(9)

Note. For both compounds the space group is  $I4/mcm$  (No. 140). The unit cell dimensions for  $\text{Sr}_3\text{GaO}_4\text{F}$  are  $a = 6.78147(5)$  Å and  $c = 11.3692(1)$  Å as determined by X-ray diffraction and  $a = 6.7819(1)$  Å and  $c = 11.3662(3)$  Å as determined by neutron diffraction. For  $\text{Sr}_3\text{AlO}_4\text{F}$  the unit cell dimensions are  $a = 6.78221(9)$  Å and  $c = 11.1437(2)$  Å.

data are also included in Table 1. The agreement between the refined model and the measured data is shown in Fig. 2. The agreement with the X-ray data is within the estimated standard deviations for the oxygen positions. Both X-ray and neutron powder diffraction patterns show a minor impurity to be present.

TABLE 2  
The Results of Madelung Site Potential (MSP) and Valence Sum Calculations as Performed with the Program Eutax (8)

Atom	X-ray data		Neutron data	
	MSP (V)	Valence sum	MSP (V)	Valence sum
$\text{Sr}_3\text{GaO}_4\text{F}$				
Sr(1)	-18.15	1.30	-18.15	1.30
Sr(2)	-19.90	2.20	-19.90	2.22
Ga	-35.25	2.98	-35.25	2.94
F	9.98	1.23	9.98	1.24
O	21.71	1.86	21.71	1.86
$\text{Sr}_3\text{AlO}_4\text{F}$				
Sr(1)	-18.44	1.38	—	—
Sr(2)	-19.48	2.15	—	—
Al	-37.59	3.68	—	—
F	10.62	1.28	—	—
O	22.00	2.02	—	—



**FIG. 3.** The structure of  $\text{Sr}_3\text{MO}_4\text{F}$  revealing the stacked  $\text{Sr}(2)\text{F}$  layers at  $z = 0$  and  $\frac{1}{2}$  that are separated by isolated  $\text{MO}_4$  tetrahedra whose oxygens coordinate the  $\text{Sr}(1)$  atoms. The strontium atoms are depicted by big grey spheres, and the fluorine atoms by small black ones. The orientation of the  $\text{MO}_4$  tetrahedra along (110) is also shown.

## RESULTS AND DISCUSSION

The crystal structure as shown in Fig. 3 is characterized by  $\text{Sr}_2\text{F}$  layers running perpendicular to the  $c$  axis and separated by isolated  $\text{GaO}_4/\text{AlO}_4$  tetrahedra which themselves are coordinating the  $\text{Sr}(1)$  atoms. The  $\text{Ga}-\text{O}$  distances within the  $\text{GaO}_4$  tetrahedra are  $1.844(2)$  Å, those within the  $\text{AlO}_4$  tetrahedra are  $1.761(4)$  Å. The tetrahedra are somewhat distorted with four  $\text{O}-\text{Ga}-\text{O}$  bond angles equal to  $114.9(2)^\circ$  and two equal to  $99.1(2)^\circ$  in  $\text{Sr}_3\text{GaO}_4\text{F}$ . The corresponding angles in  $\text{Sr}_3\text{AlO}_4\text{F}$  are  $113.8(3)^\circ$  and  $101.1(3)^\circ$ . The  $\text{Sr}(2)$  atom is coordinated by two fluorines in the  $ab$  plane. Its coordination sphere is completed by three oxygens above and by three below the  $\text{Sr}_2\text{F}$  plane. The  $\text{F}-\text{Sr}(2)-\text{F}$  angle is  $143.81(7)^\circ$  and  $144.35(6)^\circ$  for the Ga and Al compounds respectively. The bond distances about  $\text{Sr}(2)$  (see Table 3) are rather typical for a strontium in 8-fold coordination. Each fluorine is coordinated by four  $\text{Sr}(2)$  ions in the  $ab$  plane and axially by two  $\text{Sr}(2)$  ions to form an elongated octahedron of strontium about fluorine. This is confirmed by the valence sum of  $\text{Sr}(2)$  not significantly deviating from the formal oxidation state of two. The other strontium ion,  $\text{Sr}(1)$ , is embedded within the layer where the isolated  $\text{MO}_4$  tetrahedra are located. These ions are arranged in strings along the (110) direction, as are the tetrahedra, which alternate their orientation due to the mirror plane separating them. Two apical fluorine and eight oxygen ions, located on adjacent tetrahedra form the  $\text{Sr}(1)$  coordination polyhedra. The  $\text{Sr}(1)-\text{F}$  and  $\text{Sr}(1)-\text{O}$  distances are rather long for 10-coordinated strontiums. Therefore, it is not surprising that the valence sum calculations indicate

**TABLE 3**  
Bond Distances (Å) in  $\text{Sr}_3\text{GaO}_4\text{F}$  and  $\text{Sr}_3\text{AlO}_4\text{F}$

$\text{Sr}_3\text{GaO}_4\text{F}$		$\text{Sr}_3\text{AlO}_4\text{F}$	
Bond	Distance	Bond	Distance
$\text{Sr}(1)-\text{O}$	$8 \times 2.858(1)$	$\text{Sr}(1)-\text{O}$	$8 \times 2.842(4)$
$\text{Sr}(1)-\text{F}$	$2 \times 2.858(1)$	$\text{Sr}(1)-\text{F}$	$2 \times 2.786(1)$
$\text{Sr}(2)-\text{O}$	$4 \times 2.699(2)$	$\text{Sr}(2)-\text{O}$	$4 \times 2.797(4)$
	$2 \times 2.423(2)$		$2 \times 2.460(4)$
$\text{Sr}(2)-\text{F}$	$2 \times 2.523(2)$	$\text{Sr}(2)-\text{F}$	$2 \times 2.5188(8)$
$\text{Ga}-\text{O}$	$4 \times 1.844(2)$	$\text{Al}-\text{O}$	$4 \times 1.761(4)$

a substantial underbonding of  $\text{Sr}(1)$ . This may lead to a *rattling* of the  $\text{Sr}(1)$  ion within its coordination cage, which is consistent with the fact that the displacement  $B_{\text{iso}}$  of  $\text{Sr}(1)$  is significantly larger than that of  $\text{Sr}(2)$ . It also suggests that substitution with a larger isovalent ion, such as  $\text{Ba}^{2+}$ , may stabilize the structure. This also explains the preference of the smaller  $\text{Gd}^{3+}$  ion in the oxide  $\text{Sr}_2\text{GdGaO}_5$  into the eight-fold site [7].

An alternative way to describe the structure is to think of it as being made up of alternating  $\text{Sr}_2\text{F}^{3+}$  and  $\text{SrGaGO}_3^-$  ( $\text{SrAlO}_4^-$ ) layers. The large formal charge associated with each layer suggests that strong ionic interactions hold the layers together. The drive to form ionic  $\text{Sr}-\text{F}$  interactions and covalent  $\text{Ga}/\text{Al}-\text{O}$  bonds is crucial to stabilize the ordered arrangement of oxygen and fluorine.

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