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Synthesis, crystal structure and lithium ion conductivity of $LiMgFSO_4$

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Lithium magnesium fluoride sulfate, $LiMgFSO_4$, has been prepared by reaction of $MgSO_4{\cdot}H_2O$, Li_2CO_3 and NH_4F at 450–500 °C. It crystallizes in space group $P\bar{1}$ of the triclinic system, with $Z = 2$ and $a = 5.1623(7)$, $b = 5.388(1)$, $c = 7.073(1)$ Å, $\alpha = 106.68(1)$, $\beta = 107.40(1)$ and $\gamma = 97.50(1)°$. The structure is built up from single chains of corner-sharing MgO_4F_2 octahedra running parallel to the *c* axis, cross linked *via* vertex-sharing SO_4 tetrahedra, so that each tetrahedron links three different chains. Li resides within the cavities defined by the framework, wherein it is disordered between two half-occupied sites. This structure is isotypic with that of all members of the amblygonite ($LiAlFPO_4$)–montebrasite ($LiAlOHPO_4$) series, and that of tavorite ($LiFeOHPO_4$). It is topologically identical to the titanite ($CaTiOSiO_4$) and kieserite ($MgSO_4{\cdot}H_2O$) structures. The framework structure of $LiMgFSO_4$ facilitates lithium ion conduction [σ (520 °C) $= 1.5 \times 10^{-3}$ S cm^{-1}; $E_a = 0.94$ eV].

Introduction

It is now seventy years since the crystal structure of titanite (or “sphene”, $CaTiOSiO_4$), the prototypical member of the $ABXTO_4$ group of compounds, was determined by Zachariasen.[1] Since that time, considerable work has been devoted to the crystal chemistry of natural and synthetic analogs of titanite. This led to the characterization of many $ABXTO_4$ and $BXTO_4$ compounds which show the same topological arrangement of BO_4X_2 octahedra and TO_4 tetrahedra delimiting cavities which are either empty or occupied byA cations (A = Li, Na or Ca). A compilation of minerals structurally related to titanite is given in Table 11 of ref. 2 and a list of synthetic analogs is presented in Table 1.[3–14] Natural and synthetic analogs of titanite crystallize either in the monoclinic system (SG: $C2/c$ or $P2_1/c$) or in the triclinic system (SG: $P\bar{1}$); in this latter case, the structure is a slightly distorted version of the monoclinic one and, accordingly, it is frequently described in the $C\bar{1}$ space group for an easier comparison. Among compounds with the titanite structure, some monohydrated sulfates, fluoride phosphates and fluoride arsenates (see Table 11 of ref. 2) have been observed but, to our knowledge, there is no example of a fluoride sulfate. In the following, we describe the synthesis and crystal structure of a new synthetic analogue of titanite, $LiMgFSO_4$.

Table 1 Examples of synthetic analogs of titanite

Chemical formula	Space group	Reference
$NaNbOGeO_4$	$C2/c$	3, 4
$LiTaOGeO_4$	$C2/c$	3, 4
$NaTaOGeO_4$	$C2/c$	3, 4
$NaSbOGeO_4$	$C2/c$	3, 4
$LiTaOSiO_4$	$C2/c$	3, 4
$NaVOAsO_4$	$P2_1/c$	5
α-$LiTiOPO_4$	$P\bar{1}$	6
α-$LiVOPO_4$	$P\bar{1}$	7
$NaVOPO_4$	$P2_1/c$	8
α-$NaTiOPO_4$	$P2_1/c$	9
$SbOPO_4$	$P2_1/a$	10
$MnPO_4{\cdot}H_2O$	$C2/c$	11
$MnAsO_4{\cdot}H_2O$	$C2/c$	12
$LiMn(OH)AsO_4$	$C\bar{1}$	13
$LiMn(OH)PO_4$	$C\bar{1}$	14

We synthesized this solid as a part of our general effort to develop new materials exhibiting lithium ion conduction in inorganic framework materials.[15,16] Indeed, $LiMgFSO_4$ exhibits significant lithium ion conduction, comparable to that of analogues[17] $LiMn(OH)PO_4$ and $LiMn(OH)AsO_4$.

Experimental

1 Synthesis

$LiMgFSO_4$ was synthesized by heating stoichiometric quantities of the starting materials according to the reaction

$$MgSO_4{\cdot}H_2O + 1/2\ Li_2CO_3 + NH_4F \rightarrow LiMgFSO_4 + 3/2\ H_2O + 1/2\ CO_2 + NH_3 \qquad (1)$$

at 450 °C for 12 h, 500 °C for 6 h and finally at 550 °C for 6 h with intermediate grinding. For growth of single crystals, a 10% (by weight) excess of Li_2CO_3 and NH_4F was added to the reaction mixture. It was heated to 700 °C for 12 h in a Pt crucible and allowed to cool naturally.

2 Structure determination

Initial photographic work revealed triclinic symmetry and gave preliminary cell parameters that were refined from 25 reflections automatically centered on a CAD4 Enraf-Nonius diffractometer. Table 2 lists calculated interplanar distances, and the intensities calculated from the crystal structure using the program Powder Cell.[18] Single-crystal intensity data were collected, at room temperature, under the conditions given in Table 3. Data reduction and structure solution were carried out with the use of programs in the SHELXTL Plus Package[19] and the structure was refined using the JANA98 program package.[20]

Conventional atomic scattering factors and anomalous dispersion corrections were used.[21]

Table 2 X-Ray powder diffraction data[a] for $LiMgFSO_4$

h	k	l	d_{calc}/Å	I_{rel} (%)	h	k	l	d_{calc}/Å	I_{rel} (%)
0	−1	1	4.824	26	0	2	1	2.097	9
1	0	0	4.786	5	1	2	0	2.032	6
−1	0	1	4.704	35	0	−2	3	1.9878	12
1	−1	0	3.962	3	2	1	0	1.9849	26
0	1	1	3.403	20	2	−2	0	1.9812	5
−1	1	1	3.392	56	−2	0	3	1.9664	27
1	−1	1	3.328	45	2	−2	1	1.8796	3
1	0	1	3.298	25	1	−1	3	1.8476	13
0	−1	2	3.227	71	−1	−1	4	1.7637	23
−1	0	2	3.218	38	1	−2	3	1.7477	3
0	0	2	3.168	12	−2	−2	2	1.7356	2
1	1	0	3.114	100	0	2	2	1.7014	7
−1	−1	2	2.979	15	2	1	1	1.6972	3
0	−2	1	2.667	21	−2	2	2	1.6958	21
−2	0	1	2.558	33	−1	0	4	1.6933	7
−1	1	2	2.500	11	0	3	0	1.6717	23
1	−2	0	2.475	35	1	−3	2	1.6700	23
1	−1	2	2.449	6	2	−2	2	1.6641	10
0	−2	2	2.412	5	2	0	2	1.6490	24
1	1	1	2.403	11	−3	1	2	1.6302	16
2	0	0	2.393	3	0	−2	4	1.6136	14
2	−1	0	2.391	5	−2	0	4	1.6090	2
−1	0	3	2.249	2	0	−3	3	1.6079	2
0	−1	3	2.242	4	3	0	0	1.5954	14
−1	2	1	2.192	18	0	0	4	1.5839	4
−1	−2	2	2.191	2	−3	0	3	1.5679	2
−2	−1	2	2.149	10	−3	−1	2	1.5658	8
1	−2	2	2.118	3	−1	3	1	1.5637	3
2	−1	1	2.109	7	2	2	0	1.5569	11

[a] Reflections with $I_{rel} < 2\%$ have been omitted.

An absorption correction was not deemed necessary. The starting positions of all atoms were taken by analogy with those of corresponding atoms in the structure of $LiAlFPO_4$. The structure was then refined by least-squares methods, involving anisotropic displacement parameters for all atoms. Under such conditions, the U_{33} displacement parameter for Li appeared very high [0.094(9) Å^2, the equivalent isotropic displacement parameter being 0.045(5) Å^2], suggesting that Li is disordered between two discrete positions, as is the case for all members of the amblygonite ($LiAlFPO_4$)–montebrasite ($LiAlOHPO_4$) series.[2] Consequently, a split-atom model was used for Li, with two half-occupied Li positions, which were constrained to have identical isotropic displacement parameters. Using this model, the R indices were not reduced significantly, but the isotropic displacement parameter for the half-occupied Li position decreased down to a more reasonable value of 0.020(2) Å^2. The final cycle of refinement on F resulted in residuals of $R = 0.052$ and $R_w = 0.051$. Final values of the positional and displacement parameters are given in Table 4.

Table 3 Crystallographic data for $LiMgFSO_4$

Formula	$LiMgFSO_4$
Formula mass (amu)	146.3
Space group	$P\bar{1}$
a/Å	5.1623(7)
b/Å	5.388(1)
c/Å	7.073(1)
α/°	106.68(1)
β/°	107.40(1)
γ/°	97.50(1)
V/Å^3	174.72(5)
Z	2
ρ_c/g cm^{-3}	2.78
μ(Mo-Kα)/cm^{-1}	10.08
Crystal dimensions/mm	$0.2 \times 0.2 \times 0.15$
Scan mode	θ–2θ
θ limits/°	3.0–35.0
Data collected	$-8 \leqslant h \leqslant 8$, $-8 \leqslant k \leqslant 8$, $-1 \leqslant l \leqslant 11$
No. of unique data (n) with $I > 3\sigma(I)$	753
Number of variables (p)	75
$R(F)$[a]	0.0521
$R_w(F)$[b]	0.0512
$S = [\Sigma\{w(F_o - F_c)^2\}/(n-p)]^{1/2}$	1.72
$\Delta\rho_{max}$; $\Delta\rho_{min}$/e$^-$ Å^{-3})	1.05; −0.69

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$ with $w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$

Table 4 Positional and displacement parameters for $LiMgFSO_4$

Atom	Wyckoff position	Occupancy	x/a	y/b	z/c	U_{eq}[a]/Å^2 or U_{iso}*/Å^2
S	2i	1.0	0.3316(2)	0.6354(2)	0.2515(2)	0.0085(3)
Mg(1)	1b	1.0	0	0	1/2	0.0079(7)
Mg(2)	1a	1.0	0	0	0	0.0099(7)
F	2i	1.0	0.1102(4)	0.9176(4)	0.7554(3)	0.0108(8)
O(1)	2i	1.0	0.6178(5)	0.7456(5)	0.4045(5)	0.015(1)
O(2)	2i	1.0	0.1263(5)	0.6561(5)	0.3602(4)	0.011(1)
O(3)	2i	1.0	0.3177(5)	0.3525(5)	0.1448(4)	0.012(1)
O(4)	2i	1.0	0.2711(6)	0.7722(5)	0.0973(4)	0.014(1)
Li(1)	2i	0.5	0.275(4)	0.643(4)	0.789(3)	0.020(2)*
Li(2)	2i	0.5	0.253(4)	0.622(4)	0.713(3)	0.020(2)*

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\boldsymbol{U_{ij}}$ tensor.

CCDC reference number 172560. See http://www.rsc.org/suppdata/jm/b1/b108289m/ for crystallographic data in CIF or other electronic format.

3 Ionic conductivity measurement

Lithium ion conductivity was measured on a sintered pellet (sintered at 550 °C for 12 h) coated with gold paste using a HP4194A impedance/gain phase analyzer over the frequency range 100 Hz–15 MHz in the temperature range 100–525 °C in air. The measurement was made for both heating and cooling cycles. The sample was equilibrated at constant temperature for about 45 min prior to each impedance measurement and the conductivity was obtained from the low frequency intercept of the impedance plots.

Results and discussion

The crystal structure of $LiMgFSO_4$ (Fig. 1, 2 and 3) is built up from MgO_4F_2 octahedra and SO_4 tetrahedra. It can be described as consisting of chains of corner-sharing octahedra running parallel to the *c* axis, cross linked *via* vertex-sharing tetrahedra so that each tetrahedron is connected to four different octahedra, of which two belong to the same chain, *i.e.* each tetrahedron links three different chains. Each MgO_4F_2 octahedron is connected to four tetrahedra *via* the equatorial oxygen atoms and to two octahedra *via* the F anions that bridge along the length of the octahedral chain, which is kinked; the Mg(1)–F–Mg(2) angle being 133.2(1)°. Within the

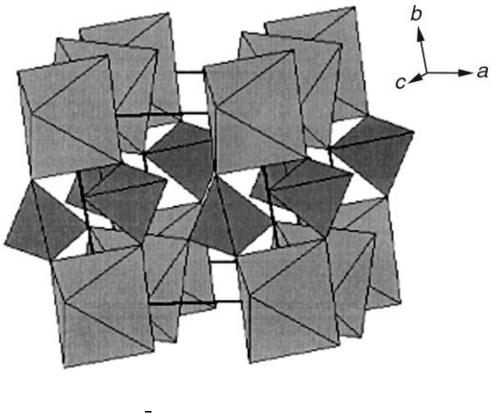

Fig. 1 Perspective [0 0 $\bar{1}$] view of the $LiMgFSO_4$ structure showing the staggered configuration of adjacent MgO_4F_2 octahedra within the octahedral chains.

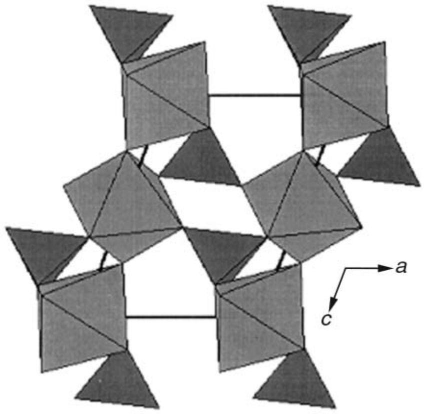

Fig. 2 [0 $\bar{1}$ 0] view of the $LiMgFSO_4$ structure.

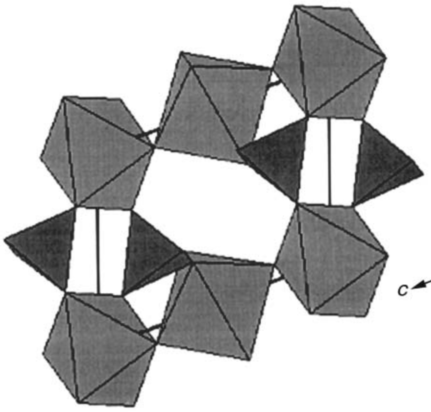

Fig. 3 [$\bar{1}$ 0 0] view of the $LiMgFSO_4$ structure.

chain, adjacent octahedra have a staggered configuration (Fig. 1). This framework delimits cavities wherein Li is disordered between two half-occupied positions.

A list of bond distances and angles is given in Table 5, along with some results of bond valence calculations.[22,23]

In the structure of $LiMgFSO_4$, there are two crystallographically distinct MgO_4F_2 octahedra, both of which have a *trans* arrangement of the F anions and are slightly flattened along the F–Mg–F direction (*i.e.* the Mg–F distances are shorter than the Mg–O). The SO_4 tetrahedron is also slightly distorted, with O–S–O angles in the range 105.3–111.4°. Due to the smaller size of this tetrahedron with respect to a PO_4 group, the Mg(1)–F–Mg(2) angle is smaller than the Al(1)–F–Al(2) angle in the structure of $LiAlFPO_4$ (133.2° instead of 139.0°), *i.e.* the octahedral chain is more kinked. However, this angle is also influenced by the size of the A cation; in the Na analog of amblygonite,[2] lacroixite ($NaAlFPO_4$),[24] the Al–F–Al angle is 142.7°.

The separation between the two split Li sites is slightly larger than that observed in amblygonite [0.49(3) Å instead of 0.41(2) Å]. Due to this splitting, the coordination environments of the Li(1) and Li(2) sites are different: Li(1) is five-coordinate (one F and four O anions) whereas Li(2) is six-coordinate (one F and five O anions), although two of the Li(2)–O bonds are rather long (see Table 5). As in the case of all members of the amblygonite–montebrasite series,[2] the splitting does not induce significant differences in the bond-valence sums around Li(1) and Li(2) with respect to the situation of an unsplit Li position. The sums are 0.906 and 0.891, respectively, suggesting that the Li atoms are loosely bound, which is also reflected by their rather high isotropic displacement factor.

We expected the framework structure and loose binding of lithium would facilitate lithium ion conduction in $LiMgFSO_4$.

Table 5 Distances (Å), angles (°) and bond valences (v. u.) for Mg(1), Mg(2), S, Li(1) and Li(2)

Mg(1)		
Mg(1)–F[a]	1.923(3)	0.387
F–Mg(1)–F	180.0	
F–Mg(1)–O(1)	89.1(1)	
F–Mg(1)–O(1)	90.9(1)	
F–Mg(1)–O(2)	86.7(1)	
F–Mg(1)–O(2)	93.3(1)	
Mg(1)–F[b]	1.923(3)	0.387
F–Mg(1)–O(1)	90.9(1)	
F–Mg(1)–O(1)	89.1(1)	
F–Mg(1)–O(2)	93.3(1)	
F–Mg(1)–O(2)	86.7(1)	
Mg(1)–O(1)[c]	2.048(3)	0.383
O(1)–Mg(1)–O(1)	180.0	
O(1)–Mg(1)–O(2)	85.2(1)	
O(1)–Mg(1)–O(2)	94.8(1)	
Mg(1)–O(1)[d]	2.048(3)	0.383
O(1)–Mg(1)–O(2)	94.8(1)	
O(1)–Mg(1)–O(2)	85.2(1)	
Mg(1)–O(2)[a]	2.118(3)	0.317
O(2)–Mg(1)–O(2)	180.0	
Mg(1)–O(2)[b]	2.118(3)	0.317
		$\Sigma = 2.174$
Mg(2)		
Mg(2)–F[e]	1.930(3)	0.389
F–Mg(2)–F	180.0	
F–Mg(2)–O(3)	89.7(1)	
F–Mg(2)–O(3)	90.3(1)	
F–Mg(2)–O(4)	84.1(1)	
F–Mg(2)–O(4)	95.9(1)	
Mg(2)–F[b]	1.930(3)	0.389
F–Mg(2)–O(3)	90.3(1)	
F–Mg(2)–O(3)	89.7(1)	
F–Mg(2)–O(4)	95.9(1)	
F–Mg(2)–O(4)	84.1(1)	
Mg(2)–O(3)	2.101(2)	0.333
O(3)–Mg(2)–O(3)	180.0	
O(3)–Mg(2)–O(4)	92.6(10)	
O(3)–Mg(2)–O(4)	87.4(1)	
Mg(2)–O(3)[f]	2.101(2)	0.333
O(3)–Mg(2)–O(4)	87.4(1)	
O(3)–Mg(2)–O(4)	92.6(1)	
Mg(2)–O(4)[a]	2.073(3)	0.357
O(4)–Mg(2)–O(4)	180.0	
Mg(2)–O(4)[g]	2.073(3)	0.357
		$\Sigma = 2.158$
S		
S–O(1)	1.467(2)	1.529
O(1)–S–O(2)	110.7(2)	
O(1)–S–O(3)	105.2(2)	
O(1)–S–O(4)	111.3(2)	
S–O(2)	1.482(3)	1.468
O(2)–S–O(3)	110.0(2)	
O(2)–S–O(4)	109.4(2)	
S–O(3)	1.475(3)	1.496
O(3)–S–O(4)	110.2(2)	
S–O(4)	1.465(4)	1.537
		$\Sigma = 6.03$
Li(1)		
Li(1)–F	1.84(2)	0.273
Li(1)–O(3)[d]	2.01(2)	0.230
Li(1)–O(4)[h]	2.10(2)	0.180
Li(1)–O(2)[b]	2.20(2)	0.138
Li(1)–O(1)[d]	2.38(2)	0.085
		$\Sigma = 0.906$
Li(2)		
Li(2)–F	1.82(2)	0.288
Li(2)–O(3)[d]	2.11(2)	0.175
Li(2)–O(2)	2.13(2)	0.166
Li(2)–O(1)[d]	2.19(2)	0.141
Li(2)–O(2)[b]	2.45(2)	0.070
Li(2)–O(4)[h]	2.57(2)	0.051
		$\Sigma = 0.891$

[a] $x, -1+y, z$; [b] $-x, 1-y, 1-z$; [c] $-1+x, -1+y, z$; [d] $1-x, 1-y, 1-z$ [e] $x, -1+y, -1+z$; [f] $-x, -y, -z$; [g] $-x, 1-y, -z$ [h] $x, y, 1+z$

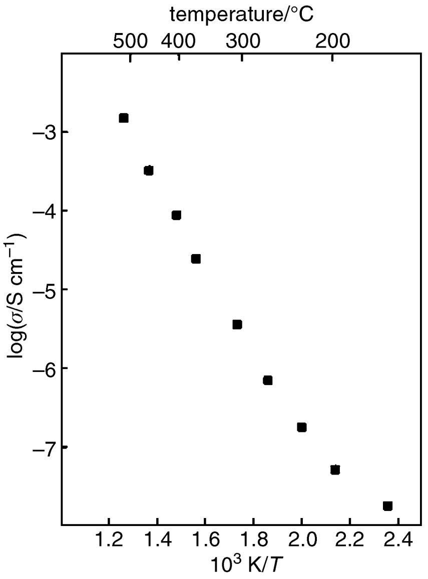

Fig. 4 Arrhenius plot for the ionic conductivity of $LiMgFSO_4$.

Indeed, $LiMgFSO_4$ exhibits significant lithium ion conduction ($\sigma = 5 \times 10^{-8}$ S cm^{-1} at 200 °C and 1.5×10^{-3} S cm^{-1} at 520 °C; $E_a = 0.94$ eV) (Fig. 4). The conductivity is comparable to that of topologically similar[17] $LiMn(OH)XO_4$ (X = P, As). Despite differences in the channel structure and lithium ion coordination between $LiMgFSO_4$ and $LiMn(OH)XO_4$ materials, there is an interesting correlation between σ/E_a and the volume per formula unit. The volume increases in the order 86.45 Å^3 [$LiMn(OH)PO_4$] < 87.36 Å^3 [$LiMgFSO_4$] < 92.55 Å^3 [$LiMn(OH)AsO_4$], while σ decreases and E_a increases in the same order. More importantly, lithium ion conduction in $LiMgFSO_4$ suggests that isostructural transition metal analogues, $LiMFSO_4$ (M = Mn, Fe, Co), would be important for redox extraction/insertion of lithium involving M^{II}/M^{III} oxidation states. Attempts are underway to synthesize $LiMFSO_4$ materials.

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