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## Two Polymorphous Lithium Stannoferrites $\text{LiFeSnO}_4$ : A Ramsdellite-Type and a Hexagonal Close-Packed Structure

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The stannoferrite  $\text{LiFeSnO}_4$  has been synthesized and investigated by X-ray diffraction and electron microscopy. Two forms have been characterized. High-temperature  $\text{LiFeSnO}_4$  is orthorhombic, isotypic with  $\text{MnO}_2$  ramsdellite:  $a = 3.066 \text{ \AA}$ ,  $b = 5.066 \text{ \AA}$ ,  $c = 9.874 \text{ \AA}$ ; low-temperature  $\text{LiFeSnO}_4$  is hexagonal with  $a = 6.012 \text{ \AA}$ ,  $c = 9.776 \text{ \AA}$  and isotypic with  $\text{Li}_{1.6}\text{Zn}_{1.6}\text{Sn}_{2.8}\text{O}_4$ . Both structures have been refined. This polymorphous transition and relationships between the two forms and spinel structure are discussed.

### Introduction

A lot of oxides with  $M_3O_4$  composition, in which several sorts of metallic atoms  $M$  can be present, are known at the present time. However, when  $M$  is characterized by a small size—i.e., an ionic radius ( $r$ ) ranging from 0.55 to 0.8  $\text{\AA}$ —a limited number of structural types is observed for these compositions. The most important classes are those of phenacite, olivine, and spinel owing to the fact that the small size of the metallic ions allows closest packing of the oxygen atoms. In a recent study (2), a hexagonal close packing of the oxygen atoms has been observed for the first time for  $\text{Sn}_{2.8}\text{Li}_{1.6}\text{M}_{1.6}\text{O}_8$  oxides ( $M = \text{Zn}, \text{Mg}$ ). Looking at the behavior of lithium and tetravalent tin, it appears that these ions are never observed together in phenacite, oli-

vine, or spinel structures. The present work deals with the structural study of the lithium stannoferrite  $\text{LiFeSnO}_4$  for which two forms have been isolated.

### Experimental

#### Synthesis

The lithium stannoferrite has been prepared from a mixture of  $\text{Li}_2\text{CO}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{SnO}_2$  corresponding to the stoichiometric ratios. This mixture is first heated for 12 hr at 600°C in order to allow the reaction of lithium carbonate with the release of carbon dioxide.

Two phases can be synthesized for this composition, depending on the thermal conditions:

—A high-temperature form (H.T.) is iso-



lated by heating the products at 900°C for 12 hr, then at 1200°C for 12 hr, and finally by quenching at room temperature.

—A low-temperature form (L.T.) is synthesized by annealing the H.T. form at 800°C.

The accurate conditions of transformation of one form to the other will be described later, in the discussion of the relations between these two forms.

#### Analysis

After each thermal treatment, the powders were ground, and studied by X-ray diffraction. The spectra of the final compounds were recorded with a Philips goniometer for the  $\text{CuK}\alpha$  radiation.

The densities were measured by pycnometry in carbon tetrachloride.

The lithium amount in the samples was determined by atomic absorption with a Varian spectrometer.

Electron diffraction study was made with a JEOL 100 CX microscope.

#### $\text{LiFeSnO}_4$ (H.T.) Ramsdellite

The high-temperature form of  $\text{LiFeSnO}_4$  is obtained in the form of a well-crystallized brown powder. The electron diffraction study of this phase showed an orthorhombic symmetry, with the reflection conditions  $hk0$  ( $h + k = 2n$ ) and  $h0l$  ( $l = 2n$ ), corresponding to the space groups  $Pm\bar{c}n$  and  $P2_1cn$ . Its X-ray diffraction pattern was thus indexed (Table I) in an orthorhombic cell with the following parameters:

$$a = 3.066(1) \text{ \AA}; b = 5.066(1) \text{ \AA}, \\ c = 9.874(2) \text{ \AA}.$$

The observed density,  $d_{\text{exp}} = 5.32$ , involves two  $\text{LiFeSnO}_4$  groups per cell ( $d_{\text{calc}} = 5.33$ ).

At this stage of the investigation, a parallel with  $\gamma\text{-MnO}_2$  ramsdellite was drawn (3) on account of the nature of the cell, despite the difference in composition. This idea

TABLE I

$|\text{LiFeSnO}_4|_{\text{HT}}$  RAMSDELLITE: CRYSTALLOGRAPHIC DATA<sup>a</sup>

$hkl$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{obs}}$	$I_{\text{calc}}$
0 0 2	4.935	4.937	3.6	5.2
0 1 1	4.509	4.507	100.0	100.0
0 1 2	3.537	3.537	1.8	2.2
0 1 3	2.761	2.760	51.9	52.0
1 1 0	2.604 <sub>0</sub>	2.623 <sub>2</sub>	32.7	34.6
1 0 2		2.604 <sub>7</sub>		
1 1 1	2.534 <sub>6</sub>	2.535 <sub>2</sub>	56.0	56.7
0 2 0		2.532 <sub>8</sub>		
0 0 4	2.468 <sub>8</sub>	2.468 <sub>4</sub>	10.7	10.4
1 1 2	2.316 <sub>6</sub>	2.316 <sub>4</sub>	9.5	9.4
0 2 2	2.252 <sub>9</sub>	2.253 <sub>3</sub>	1.5	1.8
0 1 4	2.218 <sub>1</sub>	2.219 <sub>0</sub>	2.4	1.9
1 1 3	2.008 <sub>2</sub>	2.051 <sub>3</sub>	13.7	13.5
0 2 3		1.007 <sub>2</sub>		
1 0 4	1.922 <sub>4</sub>	1.922 <sub>8</sub>	4.8	4.1
1 2 1	—	1.915 <sub>7</sub>		
1 2 2	1.816 <sub>1</sub>	1.815 <sub>9</sub>	39.3	40.7
0 2 4	1.767 <sub>3</sub>	1.767 <sub>7</sub>	17.9	17.2
1 2 3	1.679 <sub>7</sub>	1.679 <sub>4</sub>	2.1	3.1
0 3 1	1.664 <sub>6</sub>	1.664 <sub>4</sub>	3.0	2.7
0 0 6	1.645 <sub>2</sub>	1.645 <sub>6</sub>	2.4	1.7
0 3 2	1.597 <sub>4</sub>	1.597 <sub>7</sub>	1.3	1.1
1 1 5	1.577 <sub>5</sub>	1.577 <sub>6</sub>	22.0	22.0
2 0 0	1.533 <sub>0</sub>	1.533 <sub>1</sub>	10.2	10.5
1 2 4		1.531 <sub>5</sub>		
0 3 3	1.502 <sub>3</sub>	1.502 <sub>4</sub>	6.7	5.8

Note.  $a = 3.066 \text{ \AA}$ ;  $b = 5.066 \text{ \AA}$ ;  $c = 9.874 \text{ \AA}$ ;  $Z = 2$ ; spacegroup:  $Pm\bar{c}n$  or  $P2_1cn$ .

<sup>a</sup>  $d_{\text{obs}}$ ,  $d_{\text{calc}}$  and  $I_{\text{obs}}$ ,  $I_{\text{calc}}$  up to 1.50  $\text{\AA}$ .

was reinforced by the fact that the titanate  $\text{Li}_2\text{Ti}_3\text{O}_7$  synthesized by Andersson (4), has the same structure, and can have a part of its tunnels occupied by lithium, as shown by Morosin (5).

In order to verify this hypothesis, the structure of this phase was studied from powder samples. For the structure factors calculation, 71 observed reflections; i.e., 108  $hkl$  were used. All the atoms were placed in the  $4(c)$  sites of the space group  $Pm\bar{c}n$ , according to the results previously obtained for ramsdellite (5). Iron and tin atoms were randomly distributed over the octahedral sites, while lithium was statisti-

TABLE II  
 $|\text{LiFeSnO}_4|_{\text{HT}}$ : ATOMIC PARAMETERS

atom	y	z	B ( $\text{\AA}^2$ )
$\text{Li}_1: [\text{Li}_{0.25}\square_{0.75}]$	0.86(1)	0.44(1)	1
$\text{Li}_2: [\text{Li}_{0.25}\square_{0.75}]$	0.97(1)	0.57(1)	1
$B: [\text{Fe}_{0.5}\text{Sn}_{0.5}]$	0.981(2)	0.1418(4)	0.76
$\text{O}_1$	0.687(4)	0.284(2)	0.88
$\text{O}_2$	0.212(2)	-0.040(2)	0.88

Note. Space group:  $Pmcn$ ; sites  $(4c)$ :  $\frac{1}{2}yz$ .

cally distributed over two types of  $4(c)$  sites according to the results of Morosin (5) for  $\text{Li}_2\text{Ti}_3\text{O}_7$ , its isotropic thermal parameter being fixed at  $1 \text{ \AA}^2$ . Refining first the atomic positions, then the thermal parameters of tin and iron, and finally all these parameters, led to a rather low discrepancy factor,  $R_1 = 0.055$  ( $R_1 = \sum |I_0 - I_c| / \sum I_0$ ).

These results unambiguously confirm for  $\text{LiFeSnO}_4$  (H.T.) the ramsdellite structure. The atomic coordinates (Table II) of oxygen, tin, and iron are well defined. Lithium, as expected owing to its weak scattering factors, was poorly resolved in the structure analysis.

The (100) projection of the structure of

this compound, is shown on Fig. 1. The host lattice of this phase is built up of edge-sharing  $\text{SnO}_6$  and  $\text{FeO}_6$  octahedra which form rectangular tunnels running along the [100] direction. The distortion of the octahedra (Table III) is similar to that observed for  $\text{Li}_2\text{Ti}_3\text{O}_7$ : the  $\text{O}_1\text{--O}_2$  and  $\text{O}_2\text{--O}_2$  which characterize the width of a unit of two edge sharing octahedra are shorter ( $2.66\text{--}2.77 \text{ \AA}$ ), while the  $\text{O}_2\text{--O}_2$  distances between two units which characterize the width of the tunnels are much longer ( $3.39 \text{ \AA}$ ). This distortion allows the localization of the lithium ions in the tunnels. In these tunnels five sorts of sites are available for lithium: four tetrahedral sites which have been noted  $T_1$  to  $T_4$  and one octahedral site ( $\text{O}_c$ ). Taking into account the distances between two neighboring sites, four A cations per cell can be located in these tunnels leading to the limit formula  $A_4B_4\text{O}_8$  for nonstoichiometric ramsdellites  $A_xB_4\text{O}_8$  ( $0 \leq x \leq 4$ ).  $\text{LiFeSnO}_4$  and  $\text{Li}_2\text{Ti}_3\text{O}_7$  can thus be considered as partially occupied ramsdellites. The lithium titanate can be formulated  $\text{Li}_{1.72}(\text{Ti}_{3.43}\text{Li}_{0.57})\text{O}_8$ . It seems that the lithium ions are located on  $T_1$  and  $T_2$  sites, but no proof can really be drawn from this study about these light atoms. It must how-

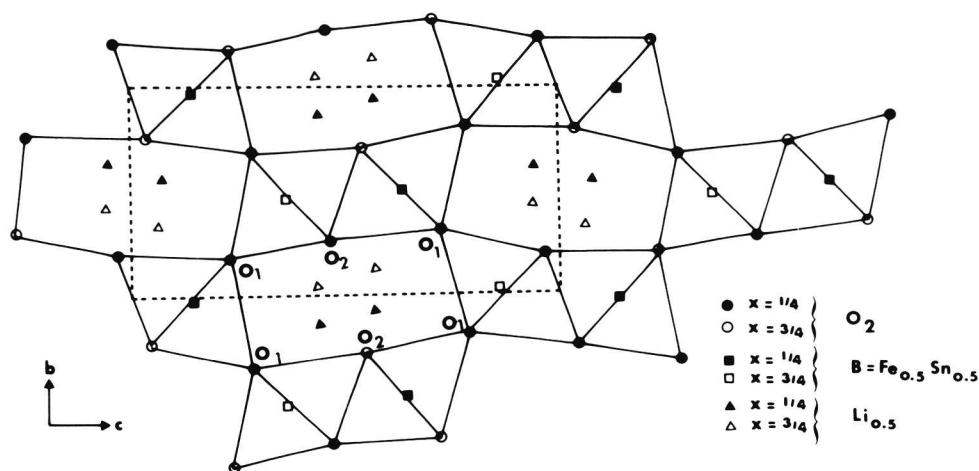


FIG. 1. Projection on to the (100) plane of the structure of  $\text{LiFeSnO}_4$ , high-temperature form.

TABLE III

|LiFeSnO<sub>4</sub>|<sub>HT</sub>: INTERATOMIC DISTANCES IN Å<sup>a</sup>

Li <sub>1</sub> -O <sub>1</sub>	1.8(1)	O <sub>1</sub> -O <sub>2</sub>   × 2	2.90(2)
Li <sub>1</sub> -O <sub>2</sub>   × 2	2.0(1)	O <sub>1</sub> -O <sub>2</sub> '  × 2	2.96(2)
Li <sub>1</sub> -O <sub>2</sub> '	2.16(10)	O <sub>1</sub> '-O <sub>2</sub>   × 2	2.66(2)
		O <sub>1</sub> '-O <sub>1</sub>   × 2	3.03(2)
Li <sub>2</sub> -O <sub>1</sub>	2.3(1)	O <sub>2</sub> '-O <sub>2</sub>   × 2	2.77(1)
Li <sub>2</sub> -O <sub>2</sub> '	1.9(1)	O <sub>1</sub> '-O <sub>1</sub>	3.066(1)
Li <sub>2</sub> -O <sub>2</sub>   × 2	2.02(7)	O <sub>2</sub> '-O <sub>2</sub> '	3.066(1)
B-O <sub>1</sub>	2.05(2)	Li <sub>1</sub> -B	2.6(1)
B-O <sub>1</sub> '  × 2	2.00(1)	Li <sub>2</sub> -B	2.4(1)
B-O <sub>2</sub>	2.15(3)	Li <sub>2</sub> -B	2.9(1)
B-O <sub>2</sub> '  × 2	2.08(1)		

<sup>a</sup> B = Fe, Sn.

ever be stated that the location of all the lithium atoms, either on T<sub>1</sub> or T<sub>2</sub>, involves a slight increase of the R factor ranging from 0.058 to 0.063 respectively. On the other hand, the localization of lithium on the other sites—T<sub>3</sub>, T<sub>4</sub>, or O<sub>c</sub>—would lead to too short Li-Fe(Sn) distances. The Li-O distances in the LiO<sub>4</sub> tetrahedra (Table III) are close to those usually observed for ternary lithium oxides, indicating that the lithium ions are strongly bound, and will not move in the tunnels.

#### Hexagonal LiFeSnO<sub>4</sub> (L.T.)

This phase is isotypic with the oxide Sn<sub>2.8</sub>Li<sub>1.6</sub>Zn<sub>1.6</sub>O<sub>8</sub> (2). Its X-ray pattern was thus indexed in a hexagonal cell with the following parameters: *a* = 6.012 (1) Å; *c* = 9.776 (2) Å (Table IV). The observed density (*d*<sub>exp</sub> = 5.29) involves 4 LiFeSnO<sub>4</sub> per cell (*d*<sub>calc</sub> = 5.33). The electron diffraction study confirmed these results and showed the reflection conditions *hhl* (*l* = 2*n*), leading to three possible space groups: *P*  $\bar{6}2c$ , *P*6<sub>3</sub>/*mmc*, and *P*6<sub>3</sub>*mc*. The *c/a* ratio equal to 1.626 indicated a hexagonal close packing of the oxygen atoms similar to those observed for A<sub>2</sub>Mo<sub>3</sub>O<sub>8</sub> (6) and Sn<sub>2.8</sub>Li<sub>1.6</sub>Zn<sub>1.6</sub>O<sub>8</sub> (2). Because of this analogy the space group *P*6<sub>3</sub>*mc* was used for the structure factors calculation.

The calculations were made on the inten-

sities of 51 observed reflections (78*hkl*). The atoms were first distributed on the positions previously obtained for Sn<sub>2.8</sub>Li<sub>1.6</sub>Zn<sub>1.6</sub>O<sub>8</sub>. Refining successively the atomic positions, the occupancy factors of the metallic sites and the thermal factors led to a discrepancy factor *R*<sub>1</sub> = 0.059. The atomic coordinates (Table V) are very close to those observed for Sn<sub>2.8</sub>Li<sub>1.6</sub>Zn<sub>1.6</sub>O<sub>8</sub>. The examination of the occupancy factor shows that tin is only located on the octahedral sites while lithium and iron are distributed on both tetrahedral and octahedral sites. Nevertheless the lithium ions are preferentially located on the tetrahedral sites (78%), while the opposite is observed for iron (22%). This distribution can be summarized in the fol-

TABLE IV

|LiFeSnO<sub>4</sub>|<sub>LT</sub>: CRYSTALLOGRAPHIC DATA<sup>a</sup>

<i>h k l</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>obs</sub>	<i>I</i> <sub>calc</sub>
1 0 0	5.211	5.207	6.0	6.9
0 0 2	4.890	4.888	21.5	22.0
1 0 1	4.594	4.595	89.5	90.5
1 0 2	3.563	3.564	58.5	58.4
1 1 0	3.006	3.006	10.2	13.6
1 0 3	2.762 <sub>3</sub>	2.762 <sub>7</sub>	63.0	63.8
2 0 0	2.604 <sub>0</sub>	2.603 <sub>3</sub>	25.6	24.8
1 1 2	2.559 <sub>7</sub>	2.560 <sub>6</sub>	103.0	102.0
2 0 1	2.515 <sub>4</sub>	2.515 <sub>6</sub>	61.3	62.1
0 0 4	2.444 <sub>2</sub>	2.444 <sub>0</sub>	11.7	10.7
2 0 2	2.297 <sub>7</sub>	2.297 <sub>2</sub>	24.6	24.5
2 0 3	2.034 <sub>0</sub>	2.033 <sub>9</sub>	35.8	36.9
2 1 1	1.928 <sub>7</sub>	1.929 <sub>2</sub>	11.0	13.0
1 1 4	1.895 <sub>7</sub>	1.896 <sub>3</sub>	5.1	6.8
1 0 5	1.830 <sub>4</sub>	1.830 <sub>1</sub>	25.5	23.5
2 1 2	1.825 <sub>1</sub>	1.825 <sub>5</sub>		
2 0 4	1.781 <sub>8</sub>	1.781 <sub>3</sub>	21.5	22.4
3 0 0	1.735 <sub>3</sub>	1.735 <sub>5</sub>	2.5	2.5
3 0 1	—	1.708 <sub>8</sub>	36.0	34.6
2 1 3	1.683 <sub>9</sub>	1.684 <sub>6</sub>		
3 0 2	1.634 <sub>9</sub>	1.635 <sub>5</sub>	24.3	27.1
0 0 6	—	1.629 <sub>3</sub>		
2 0 5	1.563 <sub>1</sub>	1.563 <sub>4</sub>	61.8	57.9
1 0 6	1.555 <sub>2</sub>	1.555 <sub>0</sub>		
2 2 0	1.502 <sub>8</sub>	1.503 <sub>0</sub>	42.2	41.5

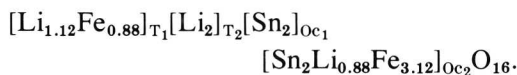
Note. *a* = 6.012 Å; *c* = 9.776 Å; *Z* = 4, space group: *P*6<sub>3</sub>*mc*.

<sup>a</sup> *d*<sub>obs</sub>, *d*<sub>calc</sub> and *I*<sub>obs</sub>, *I*<sub>calc</sub> up to 1.50 Å.

TABLE V  
 $[\text{LiFeSnO}_4]_{\text{LT}}$ : ATOMIC PARAMETERS

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ( $\text{\AA}^2$ )
$[\text{Sn}]_{\text{Oc}_1}$	2( <i>b</i> )	$\frac{1}{3}$	$\frac{2}{3}$	0.497(1)	0.1
$[\text{Li, Fe, Sn}]_{\text{Oc}_2}$	6( <i>c</i> )	0.167(1)	-0.167(1)	0.214(2)	0.9
$[\text{Li, Fe}]_{\text{T}_1}$	2( <i>b</i> )	$\frac{1}{3}$	$\frac{2}{3}$	-0.082(6)	2.0
$[\text{Li}]_{\text{T}_2}$	2( <i>a</i> )	0	0	0.51(1)	2.5
$\text{O}_1$	2( <i>a</i> )	0	0	0.325(5)	1.0
$\text{O}_2$	2( <i>b</i> )	$\frac{1}{3}$	$\frac{2}{3}$	0.107(3)	0.6
$\text{O}_3$	6( <i>c</i> )	0.481(2)	-0.481(2)	0.342(3)	1.6
$\text{O}_4$	6( <i>c</i> )	0.160(6)	-0.160(6)	0.612(3)	0.4

lowing manner:



This structure can be described as a stacking along *c* of two sorts of layers: octahedral layers [Oc] and mixed layers [ $\text{T}_2\text{Oc}$ ] formed of tetrahedra and octahedra. These layers have already been described (2) but it must be outlined that they are identical to the two sorts of layers forming the spinel structure. Both structures, spinel and hexagonal  $\text{LiFeSnO}_4$  differ only by the stacking of these layers, which changes from ABCABC in the spinel to ABACABAC in this structure. The interatomic distances (Table VI) are close to those usually observed for these compounds, and agree with the relative sizes of the ions. Some distances between cations are rather short: 3.021  $\text{\AA}$  between octahedral sites  $\text{Oc}_2$  and 2.635  $\text{\AA}$  between  $\text{T}_2$  and  $\text{Oc}_2$  sites.

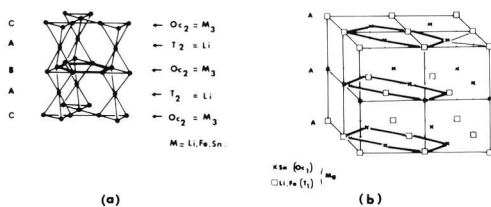


FIG. 2. Idealized drawings of: (a) the cationic  $\text{LiM}_3$  lattice of hexagonal  $\text{LiFeSnO}_4$  structure, showing up the hexagon of Kagôme planes; (b) the  $|\text{Oc}_1\text{-T}_1|$  lattice.

The cationic array of  $\text{LiFeSnO}_2$  can be compared with that of spinel  $\text{AB}_2\text{O}_4$ . The two types of layers, octahedral layers [Oc] which form a Kagôme lattice and mixed layers [ $\text{T}_2\text{Oc}$ ] formed of tetrahedra and octahedra, are found in both structure. But, while the cationic lattice of the spinel structure corresponds to the  $\text{C}_{15}$  structural type of Laves phases, i.e.,  $\text{MgCu}_2$ , as shown by Joubert (7), the cations in  $\text{LiFeSnO}_4$  form a  $\text{C}_{14}$  type Laves phase, corresponding to the  $\text{MgZn}_2$  structure (8). The  $[\text{Li}_2]_{\text{T}_2}[\text{Sn}_2\text{Li}_{0.88}\text{Fe}_{3.12}]_{\text{Oc}_2}$  lattice, built up from  $\text{LiM}_3$  tetrahedra ( $M = \text{Li, Fe, Sn}$ ) is in fact the  $\text{Zn}_2\text{Mg}$  (Fig. 2a) and the  $[\text{Li}_{1.12}\text{Fe}_{0.88}]_{\text{T}_1}[\text{Sn}_2]_{\text{Oc}_1}$  lattice corresponds to

TABLE VI  
 $[\text{LiFeSnO}_4]_{\text{LT}}$ : INTERATOMIC DISTANCES IN  $\text{\AA}$

$ \text{Oc}_1\text{-O}_3  \times 3$	2.18(2)	$ \text{T}_2\text{-Oc}_2  \times 3$	2.64(8)
$ \text{Oc}_1\text{-O}_4  \times 3$	2.11(3)	$ \text{Oc}_2\text{-Oc}_2  \times 2$	3.02(1)
$ \text{Oc}_2\text{-O}_1  \times 1$	2.05(2)	$ \text{Oc}_2\text{-Oc}_2  \times 2$	2.99(1)
$ \text{Oc}_2\text{-O}_2  \times 1$	2.02(2)	$ \text{O}_1\text{-O}_3  \times 6$	3.06(9)
$ \text{Oc}_2\text{-O}_3  \times 2$	2.06(2)	$ \text{O}_1\text{-O}_4  \times 3$	3.27(5)
$ \text{Oc}_2\text{-O}_4  \times 2$	1.99(3)	$ \text{O}_1\text{-O}_4  \times 3$	2.68(5)
		$ \text{O}_2\text{-O}_3  \times 3$	2.77(3)
$ \text{T}_1\text{-O}_2  \times 1$	1.86(6)	$ \text{O}_2\text{-O}_3  \times 3$	3.23(3)
$ \text{T}_1\text{-O}_3  \times 3$	2.06(3)	$ \text{O}_2\text{-O}_4  \times 6$	3.01(4)
$ \text{T}_2\text{-O}_1  \times 1$	1.84(10)	$ \text{O}_3\text{-O}_3  \times 2$	2.68(2)
$ \text{T}_2\text{-O}_4  \times 3$	1.94(10)	$ \text{O}_3\text{-O}_4  \times 2$	3.13(4)
		$ \text{O}_3\text{-O}_4  \times 2$	2.92(4)
		$ \text{O}_4\text{-O}_4  \times 2$	3.10(4)
		$ \text{O}_4\text{-O}_4  \times 2$	2.91(4)

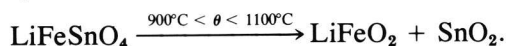
that of magnesium in this structure (Fig. 2b).

### Phase Transition and Structural Relations

In order to determine the nature of the phase transition observed for  $\text{LiFeSnO}_4$ , the thermal stability of these compounds was investigated, and the structural relations were studied.

#### Thermal Stability

High-temperature  $\text{LiFeSnO}_4$  with ramsdellite structure can only be obtained by quenching it from  $1200^\circ\text{C}$  to room temperature. Annealing this phase for several days at temperatures ranging from  $900$  to  $1100^\circ\text{C}$ , involves decomposition according to the equation:



Low-temperature hexagonal  $\text{LiFeSnO}_4$  cannot be synthesized by direct action of  $\text{Li}_2\text{CO}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{SnO}_2$ . It is only obtained by annealing H.T. ramsdellite at  $800^\circ\text{C}$ . The kinetics of this reaction are very fast: a complete transformation is observed within a few hours at this temperature. The L.T. phase is metastable: its stability range versus temperature and reaction time is very narrow. Decomposition to  $\text{LiFeO}_2$  and  $\text{SnO}_2$  is observed above  $880^\circ\text{C}$ , and prolonged annealings even at lower temperature, for example several days at  $700^\circ\text{C}$  result in the same decomposition.

#### Structural Relationships

Comparing the cell parameters of the ramsdellite (H.T.) form and those of the hexagonal L.T. form, shows the following relations:

$$a_r \approx a_h/2; \quad b_r \approx a_h 3^{1/2}/2; \quad c \approx c_h.$$

From these relations it appears that the ratios:

$$\frac{c_r}{2a_r} = 1.61 \quad \text{and} \quad \frac{c_r}{2b_r/3^{1/2}} = 1.69$$

are very close to the  $c/a$  ratio observed for an hexagonal close packing of oxygen atoms. The distribution of the oxygen atoms in the (001) plane of ramsdellite shows that each oxygen layer is very similar to that observed for hexagonal  $\text{LiFeSnO}_4$ : it can be considered as a slightly puckered close packed hexagonal layer. Comparison of both projections on to the (100) plane for ramsdellite (Fig. 3a) and (210) plane for hexagonal form (Fig. 3d) shows that the stacking along  $c$  of the oxygen layers are similar in both structures, corresponding to the ABAC sequence. The oxygen framework of ramsdellite differs only from that of hexagonal  $\text{LiFeSnO}_4$  by a slight displacement of two adjacent layers. In spite of the existence of tunnels, ramsdellite can thus be considered as having a nearly close-packed oxygen framework: the volume occupied by one unit  $\text{LiFeSnO}_4$  is indeed very similar in both structures:  $153.35 \text{ \AA}^3$  in ramsdellite and  $153 \text{ \AA}^3$  in the hexagonal form. The main difference between these structures concerns the distribution of the metallic ions, so that the hexagonal form could be considered as strongly related to a tunnel structure.

This is easily explained by imagining an hypothetical structure (Fig. 3c) intermediate between the two forms; this structure is obtained only by compressing the ramsdellite structure along  $c$  forming tunnels characterized by  $60$ – $120^\circ$  angles, where lithium ions could be located. The transition from this hypothetical structure to the hexagonal  $\text{LiFeSnO}_4$  concerns only the migration of the metallic ions through the oxygen framework.

It is possible to describe the transition ramsdellite–hexagonal form as a transition between two semioordered states of the cationic lattice, involving a slight displacement of the oxygen atoms. Possibility of existence of intermediate structures corresponding to different cationic orders, as that described for the hypothetical struc-

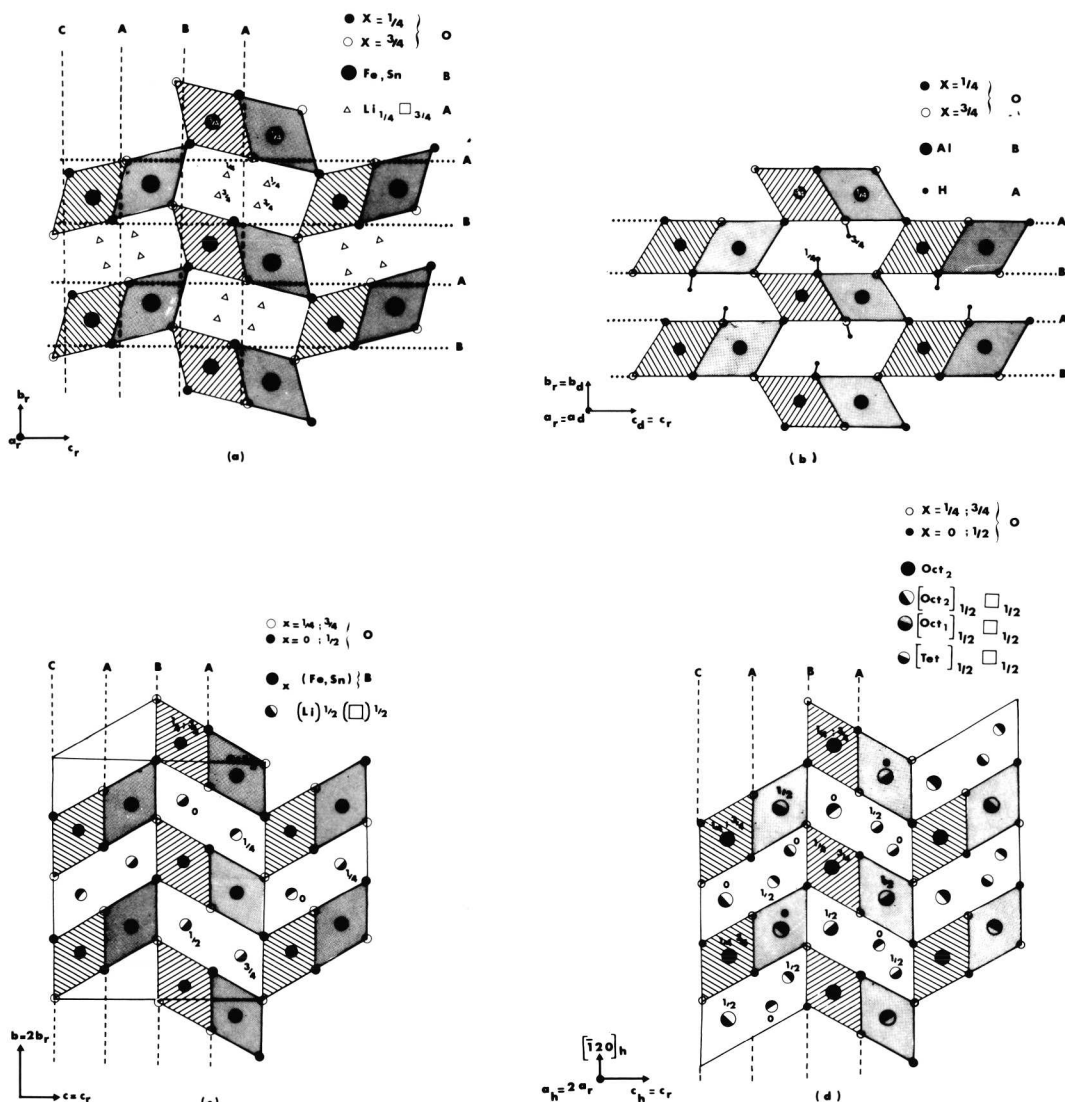


FIG. 3. Idealized projections of: (a) ramsdellite  $|\text{LiFeSnO}_4|_{\text{HT}}$ ; (b) diaspore  $\text{AlO}(\text{OH})$ ; (c) hypothetical "antidiaspore" with  $\text{LiFeSnO}_4$  formula; (d) hexagonal  $|\text{LiFeSnO}_4|_{\text{LT}}$ .

ture, can be considered. During this study superstructures have in fact been observed by electron diffraction as well as X-ray diffraction at different temperatures, but unfortunately none of these phases could be isolated.

Attention must be drawn on the relationships between these structures and  $\text{AlO}(\text{OH})$  diaspore. The tunnels of the hy-

pothetical structure proposed here are identical to those observed in diaspore. The diaspore framework (Fig. 3b) can in fact be obtained from ramsdellite by expansion of the structure along  $c$ , so that the hypothetical structure can be considered as an "antidiaspore" structure. This similarity of ramsdellite with diaspore is better understood if it is observed that ramsdellite is



characterized by another series of rather distorted hexagonal close packed oxygen layers parallel to (001), whose stacking along **b** (Fig. 3a) allows, by expansion along **c**, to form the ABAB hexagonal close packing observed in diaspore (Fig. 3b).

### Conclusion

A ramsdellite structure, corresponding to the same composition as spinel phases  $AB_2O_4$ , has been observed for the first time. These structural results show strong relationships between the  $LiFeSnO_4$  ramsdellite, hexagonal  $LiFeSnO_4$  and spinel structures. This polymorphous transition, which has never been observed in the  $AB_2O_4$  oxides (10) to our knowledge, can be compared with the order-disorder phenomena reported for numerous type oxides such as antimonates  $M_4M'SbO_8$  (11).

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