

STRUCTURE OF INORGANIC  
COMPOUNDS

Synthesis, Crystal Structure, and Magnetic Properties  
of a  $\text{Li}_8\text{FeSm}_{22}\text{O}_{38}$  Single Crystal

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Received May 25, 2011

**Abstract**—  $\text{Li}_8\text{FeSm}_{22}\text{O}_{38}$  single crystals have been grown by spontaneous flux crystallization, and their structure has been identified by X-ray diffraction analysis as follows: cubic crystals,  $a = 11.9078(5)$  Å, sp. gr.  $Im\bar{3}m$ ,  $Z = 2$ . Fe atoms occupy two mixed positions. Magnetic ions have different ligand environments: a regular octahedron  $(\text{Sm}/\text{Fe})\text{O}_6$ , a three-cap trigonal prism  $\text{SmO}_9$ , and a square antiprism  $\text{SmO}_8$ . The rather low Neel temperature ( $\sim 3$  K) can be explained by the considerable variation in the angles and lengths of exchange couplings between magnetic ions.

**DOI:** 10.1134/S1063774512060065

Oxide crystals of  $3d$ - and  $4f$ -elements are of interest due to the variety of their physical, in particular, magnetic properties. Such compounds include high temperature superconductors, multiferroics, ferrites, and materials with giant magnetoresistivity. A variety of magnetic properties are associated with the difference in the electronic structures of  $3d$ - and  $4f$ -elements, which leads to the formation of different types of magnetic order and a variety of magnetic properties. Therefore, synthesis and investigation of new compounds of this family is an urgent problem. In this study, we synthesized for the first time  $\text{Li}_8\text{FeSm}_{22}\text{O}_{38}$  single crystals and studied their crystal structure and magnetic properties.

Crystals were grown by spontaneous flux crystallization using furnaces with silit heaters. The temperature conditions were controlled by an RTP programmer with an error of  $\pm 0.1^\circ\text{C}$ .  $\text{Sm}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Li}_2\text{CO}_3$  oxides were used as the initial charge; they were preliminarily desiccated in a drying box and then thoroughly mixed in an agate mortar. The flux was prepared by joint melting of the starting charge components in a platinum crucible. The onset of charge melting was determined visually. When a “mirror” appeared on the surface, the temperature was raised by  $30^\circ\text{C}$  and the flux was homogenized for 1 h. Then the temperature was lowered until several nucleation centers arose on the surface, and further cooling from the maximum temperature  $t_{\text{max}} = 1200$  to  $t_{\text{min}} = 900^\circ\text{C}$  was performed at a rate of  $3.6^\circ\text{C}/\text{h}$  to complete crystallization of the melt surface. Single crystals in the form of black plates  $4 \times 3 \times 1$  mm<sup>3</sup> in size were extracted from the crucible by boiling in a weak nitric acid solution.

The basic crystallographic characteristics, experimental details, and parameters of structure solution and refinement are listed in Table 1.

**Table 1.** Crystallographic characteristics, experimental details, and solution and refinement parameters of the  $\text{Li}_{15.9}\text{Fe}_{2.1}\text{Sm}_{43.6}\text{O}_{76}$  structure

<i>M</i>	7998.89
System, sp. gr., <i>Z</i>	Cubic, $Im\bar{3}m$ , 2
<i>a</i> , Å	11.9078(5)
<i>V</i> , Å <sup>3</sup>	1688.47(7)
<i>D<sub>x</sub></i> , g/cm <sup>3</sup>	7.867
Radiation; λ, Å	$\text{MoK}\alpha$ , λ = 0.7107 Å
μ, mm <sup>-1</sup>	37.77
<i>T</i> , K	300
Sample sizes, mm	0.15 × 0.20 × 0.35
Diffractometer	SMART APEXII
Scanning type	ω
Absorption correction; <i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	Multiscanning, 0.3014, 0.7459
θ <sub>max</sub> , deg	29.72
Ranges of indices <i>h</i> , <i>k</i> , <i>l</i>	$-16 \leq h \leq 16$ , $-16 \leq k \leq 15$ , $-16 \leq l \leq 16$
Number of reflections measured/number of unique reflections ( <i>N</i> <sub>1</sub> ), <i>R</i> <sub>int</sub> /number of observed reflections with $I > 2\sigma(I)$ ( <i>N</i> <sub>2</sub> )	7729/273, 0.071/266
Number of parameters refined	18
Extinction correction, coefficient	SHELX97, 0.0012(2)
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> for <i>N</i> <sub>1</sub>	0.046/0.1304
<i>R</i> <sub>1</sub> for <i>N</i> <sub>2</sub>	0.0401
<i>S</i>	1.146
Δρ <sub>min</sub> /Δρ <sub>max</sub> , e/Å <sup>3</sup>	-1.04/1.28
Programs for refinement	SHELXS [1], SHELXL [2]

**Table 2.** Atomic coordinates, position occupancies  $q$ , and equivalent thermal parameters  $U_{\text{eq}}$  ( $\text{\AA}^2$ ) for Sm3 and Sm4 and isotropic parameters  $U_{\text{iso}}$  ( $\text{\AA}^2$ ) for other atoms

Atom	$x$	$y$	$z$	$q$	$U_{\text{eq}}/U_{\text{iso}}$
Fe1	0	0	0	0.42	0.008(1)
Sm1	0	0	0	0.58	0.008(1)
Fe2	1/4	1/4	1/4	0.16	0.0041(6)
Sm2	1/4	1/4	1/4	0.84	0.0041(6)
Sm3	0	0.30950(8)	0.30950(8)	1.0	0.0135(6)
Sm4	0.3475(1)	0	0	1.0	0.0041(5)
O1	0	0.156(3)	0	0.8(1)	0.02(1)
O2	0.3606(7)	0.3606(7)	0.191(1)	1.0	0.010(2)
O3	1/4	1/2	0	0.5	0.009(9)
O4	0.133(3)	1/2	0	0.5	0.006(6)
Li	0.125(2)	0.125(2)	0.875(2)	1.0	0.010(5)

The structure model was found by the direct method. An analysis of the coordination and bond lengths of the four polyhedra obtained showed that Fe atoms can occupy only the (0,0,0) and (1/4,1/4,1/4) positions. However, refinement showed that these positions can also be occupied by Sm atoms. We could not refine the Fe/Sm occupancy of these positions because of a refinement instability. Therefore, we first refined the occupancy of these positions as containing only Sm atoms and then completed the occupancy with Fe atoms. An analysis of the structure showed that O3 and O4 atoms are located close to each other (at a distance of 1.4 Å); i.e., these are two positions of one disordered oxygen atom. It was also revealed that the O1 position is occupied incompletely. The atomic coordinates and occupancies of atomic positions are listed in Table 2, and the main interatomic distances are given in Table 3. The structure is shown in Fig. 1.

The final structure refinement in the anisotropic approximation for Sm3 and Sm4 atoms and in the isotropic approximation for the remaining atoms led to

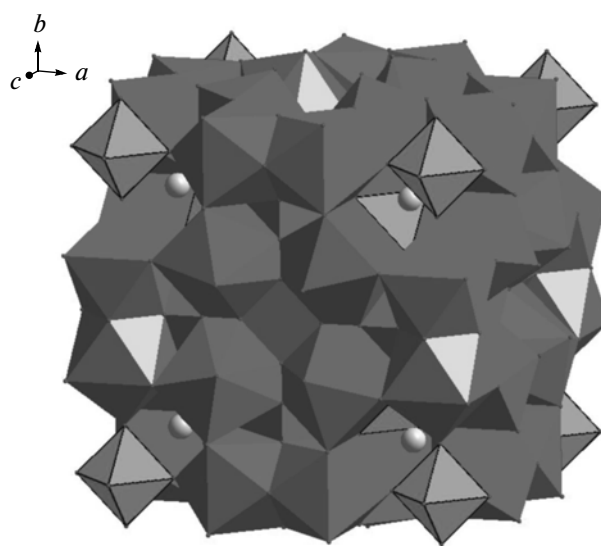
**Table 3.** Basic interatomic distances  $d$ , Å

(Sm1/Fe1)—O1 × 6	1.8368(1)
(Sm2/Fe2)—O2 × 6	2.0123(1)
Sm3—O3 × 2	2.3771(1)
Sm3—O4 × 2	2.3827(1)
Sm3—O2 × 2	2.4471(1)
Sm3—O2 × 4	2.6208(1)
Sm4—O1 × 1	2.2998(1)
Sm4—O2 × 4	2.3679(1)
Sm4—O4 × 4	2.3840(1)

the formula  $\text{Li}_{15.9}\text{Fe}_{2.1}\text{Sm}_{43.6}\text{O}_{76}$ , which transforms to  $\text{Li}_8\text{FeSm}_{22}\text{O}_{38}$  after cancellation and rounding.

The  $\text{Li}_8\text{FeSm}_{22}\text{O}_{38}$  structure has a three-dimensional framework construction. Its basic elements are two independent octahedra (Sm/Fe) $\text{O}_6$ ; a trigonal prism  $\text{LiO}_6$ ; and two types of Sm-containing polyhedra: a three-cap trigonal prism (Sm4) $\text{O}_9$  and a square antiprism (Sm3) $\text{O}_8$ , one vertex of which is disordered in two positions, each with an occupancy of 0.5 (O3 and O4 atoms).

The (Sm1/Fe1) $\text{O}_6$  octahedra share a face with the  $\text{LiO}_6$  trigonal prism, whose opposite face is shared with the (Sm2/Fe2) $\text{O}_6$  octahedra. The opposite face of

**Fig. 1.** Structure of  $\text{Li}_8\text{FeSm}_{22}\text{O}_{38}$  crystal: (Sm1/Fe1) $\text{O}_6$  and (Sm2/Fe2) $\text{O}_6$  octahedra, Sm3 and Sm4 eight- and nine-vertex polyhedral, and Li atoms (grey circles).



**Fig. 2.** Sm1/Fe1–Li–Sm2/Fe2–Li–Sm1/Fe1 chains in the  $\text{Li}_8\text{FeSm}_{22}\text{O}_{38}$  structure. Octahedra and prisms are  $(\text{Sm}/\text{Fe})\text{O}_6$  and  $\text{LiO}_6$  polyhedra, respectively.

the  $(\text{Sm}2/\text{Fe}2)\text{O}_6$  octahedra is also shared with the other symmetrically equivalent  $\text{LiO}_6$  polyhedron. Thus, chains of polyhedra with shared faces are implemented along four threefold axes in the form  $-(\text{Sm}1/\text{Fe}1)\text{O}_6-\text{LiO}_6-(\text{Sm}2/\text{Fe}2)\text{O}_6-\text{LiO}_6-(\text{Sm}1/\text{Fe}1)\text{O}_6$ ; therefore, the  $(\text{Sm}1/\text{Fe}1)\text{O}_6$  and  $(\text{Sm}2/\text{Fe}2)\text{O}_6$  octahedra have no shared vertices but are connected via a Li ion (Fig. 2). The  $(\text{Sm}1/\text{Fe}1)\text{O}_6$  octahedron has six faces shared with  $\text{LiO}_6$  prisms, while the  $(\text{Sm}1/\text{Fe}1)\text{O}_6$  octahedron has only two such faces.

In addition, the  $(\text{Sm}1/\text{Fe}1)\text{O}_6$  octahedron shares a vertex with the  $(\text{Sm}4)\text{O}_9$  polyhedron. The  $(\text{Sm}4)\text{O}_9$  polyhedron, in turn, shares a face with a symmetrically equivalent  $(\text{Sm}4)\text{O}_9$  polyhedron. Thus, chain of polyhedra are implemented along three fourfold axes in the form  $(\text{Sm}1/\text{Fe}1)\text{O}_6-(\text{Sm}4)\text{O}_9-(\text{Sm}4)\text{O}_9-(\text{Sm}1/\text{Fe}1)\text{O}_6$ .

The  $(\text{Sm}2/\text{Fe}2)\text{O}_6$  octahedron shares two faces with  $\text{LiO}_6$  prisms, and its other six faces are shared with six symmetrically equivalent  $(\text{Sm}3)\text{O}_8$  square antiprisms.

The magnetic susceptibility of crystal was measured on an MPMS device in the temperature range of 2–24 K and on a SQUID magnetometer in a field of 5 kOe. The temperature of the magnetic transition was found to be about 3 K. The asymptotic Curie temperature is negative in all cases, which indicates that negative exchange interactions dominate in this crystal. A rather low Neel temperature can be explained by the considerable variation in the angles and lengths of exchange couplings between magnetic ions.

The resonance properties of  $\text{Li}_8\text{FeSm}_{22}\text{O}_{38}$  crystal were studied in the temperature range of 100–300 K on a Bruker Elexsys E580 spectrometer operating in the X-ray wavelength range.

A single line of Lorentz shape was observed in the entire temperature range; its parameters were as follows:  $g$ -factor = 2.016 and linewidth  $\Delta H = 250$  Oe at room temperature.

We are planning to study the crystal structure at low temperatures to find out if there are structural phase transitions.

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*Translated by T. Dmitrieva*