

LiFeSnO₄ : A NEW POLYMORPHOUS TRANSITION BETWEEN A HEXAGONAL CLOSE PACKED STRUCTURE AND A RAMSDELLITE TYPE

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ABSTRACT

A new polymorphous transition is observed for lithium stannoferrites LiFeSnO₄. Two forms have been characterized and studied by means of X-ray diffraction and electron microscopy : the high temperature form is orthorhombic, isotypic with γ-MnO₂ ramsdellite and the low temperature form is double hexagonal (ABAC), isotypic with Sn_{1.4}Li_{0.8}Mn_{0.8}O₄. Both structures have been refined. This polymorphous transition and relationships between the two forms and spinel structure are discussed.

INTRODUCTION

A new structural type, with M₃O₄ formula, characterized by a hexagonal close packing of the oxygen atoms was recently obtained for the lithium stannates Sn_{1.4}Li_{0.8}Mn_{0.8}O₄ (ref. 1). The present work deals with the structural study of LiFeSnO₄ for which a polymorphous transition is observed and the relationships between the two structures obtained and the spinel.

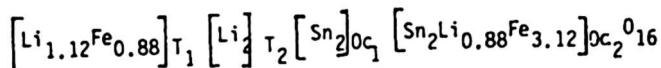
CRISTALLOGRAPHIC DATA

Two phases LiFeSnO₄ can be synthesized, depending on the thermal conditions - an orthorhombic high temperature form with a ramsdellite type structure (ref.

2) a = 3.066 Å, b = 5.066 Å and c = 9.874 Å with the space groups Pmcn and P2₁cn. The structure was studied from powder samples (R_f = 0.055) ; the iron ions and tin atoms are randomly distributed over the octahedral sites while the lithium are supposed to be statistically distributed over two types of tetrahedral sites in the tunnels. A neutron diffraction study is in progress for determining the exact location of Li⁺.

- a double hexagonal (ABAC) low temperature form, (DH) LiFeSnO₄, only obtained by annealing ramsdellite form at 870°C, with the following parameters : a = 6.012 Å and c = 9.776 Å with the space groups P₆2c, P₆₃/mmc and P₆₃mc. The

structure calculations ($R_1 = 0.059$) show an isotypism with $\text{Sn}_{1.4}\text{Li}_{0.8}\text{M}_{0.8}\text{O}_4$ oxides. The ionic distribution can be summarized in the following manner :



PHASE TRANSITION AND STRUCTURAL RELATIONS

The ramsdellite structure of LiFeSnO_4 has a nearly hexagonal close packing of the oxygen atoms as it appears from the ratios $c_r/2a_r = 1.61$ and $c_r/2b_r \sqrt{3} = 1.69$. Figure 1 a shows the sequence of close packing along the \vec{b}_r and \vec{c}_r axis.

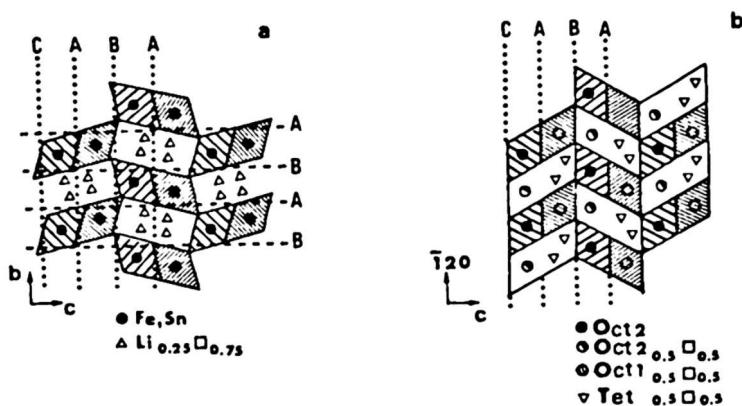


Fig. 1. Idealized projection of the two forms of LiFeSnO_4 : a) ramsdellite viewed along a_r . b) double hexagonal viewed along a_H .

Ramsdellite structure can lead to two types of hypothetical close packed structures : an (ABAB) by expansion of the structure along \vec{c}_r and an (ABAC) sequence similar to that of $(\text{DH})\text{LiFeSnO}_4$ by expansion along \vec{b}_r . The main difference between the ramsdellite and the double hexagonal LiFeSnO_4 structures concerns the distribution of the metallic ions. It is possible to describe the transformation as a transition between the semi-ordered states of cationic lattice involving a slight displacement of the oxygen atoms (Fig. 1a, b).

In terms of polyhedra arrangement, the double hexagonal structure of LiFeSnO_4 can be described as an alternate stacking along \vec{c}_H of two sorts of layers : octahedral, "kagome" (ref. 3) layers $[\text{O}_3]$ and mixed layers $[\text{Te}_2\text{O}_\text{C}]$ (Fig. 2a, b).

It must be outlined that they are identical to those forming the spinel structure and that, in both structures, two successive layers are always $[\text{O}_3]$ and $[\text{Te}_2\text{O}_\text{C}]$. These "double-layers" $[\text{O}_3\text{Te}_2\text{O}_\text{C}]$ allow to describe $(\text{DH})\text{LiFeSnO}_4$

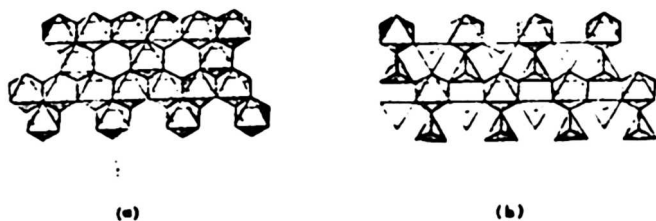


Fig. 2. Idealized polyhedral layers of (DH)LiFeSnO₄ : a) [Oc₃] kagome layer. b) [Fe₂Oc] mixed layer.

(Fig. 3) and spinel structures. The relationships study is in progress.

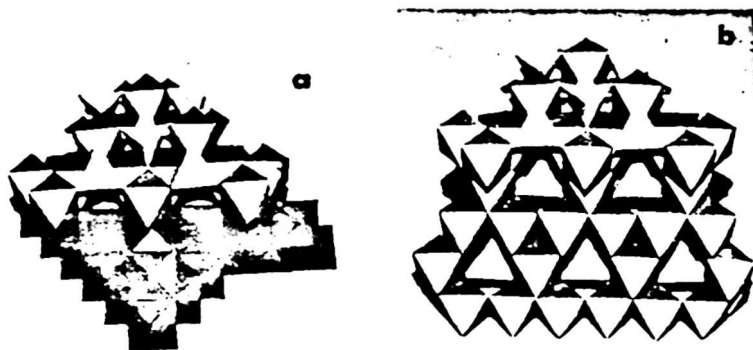


Fig. 3. a) double hexagonal structure of LiFeSnO₄, low temperature form, built up alternately from two octahedral layers and two mixed layers. b) spinel structure built up from three double-layers [Oc₃Te₂Oc].

The tunnels of the ramsdellite form of LiFeSnO₄ are only occupied by a small amount of light atoms, Li⁺, allowing the possibility of direct imaging by electron microscopy. Figure 4 presents a micrography of a thin crystal viewed along the a axis ; a comparison between the structural model and the image shows a one-to-one correspondance between the white spots and the position of the tunnels in the structure.

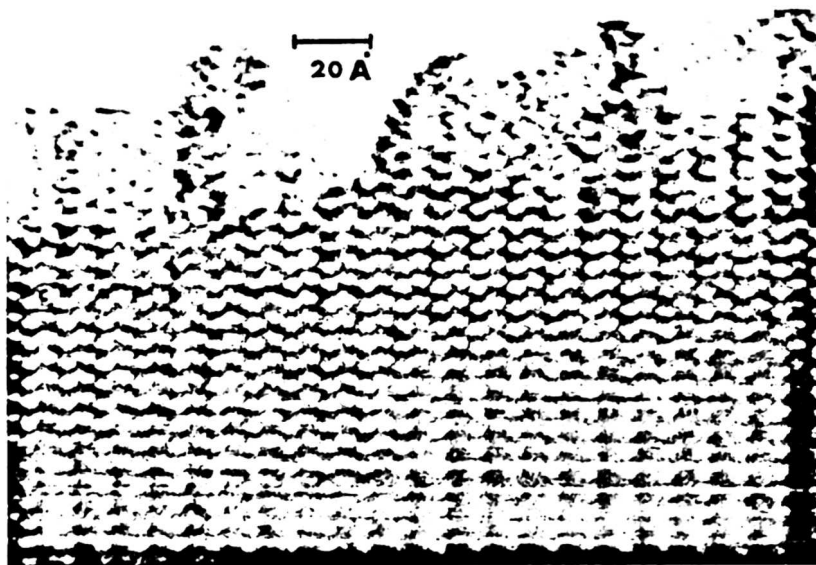


Fig. 4. High resolution micrography of the ramsdellite form of LiFeSnO_4 viewed along the a axis.

CONCLUSION

A polymorphous transition, ramsdellite-double hexagonal, has been observed for the first time for the lithium ferrostannate LiFeSnO_4 , corresponding to the same composition as spinel phases, AB_2O_4 . These structural results show up new relations between the high temperature form, ramsdellite, of LiFeSnO_4 , related to close packed structures, double hexagonal low temperature form and spinel structures, requiring a more elaborate study.

REFERENCES

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