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Crystal Structure and Magnetic Properties of a Platelet-Shaped (Li, Zn) Spinel Ferrite, Obtained by Ion Exchange from β'' Alumina-like Ferrite

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Room-temperature crystal structure of a new spinel (formula: $Li_{0.75}Fe_{4.75}Zn_{0.5}O_8$) obtained by ionic exchange from β'' ferrite compound (formula: $Na_{1.3}K_{0.6}Fe_{10.1}Zn_{0.9}O_{17}$) is refined from X-ray single crystal data. The compound is cubic (space group $P4_332$) with cell parameter a = 8.239(1) Å. Crystal structure and distribution of Li, Zn, and Fe cations among the different crystallographic sites have been determined. Magnetic properties and influence of annealing have been studied. Coercive field reaches a value up to 134 Oe for a crystallite size lower than 0.2 μ, as a consequence of a strong shape anisotropy.

1. Introduction

β'' alumina related materials are excellent ionic conductors. Isostructural compounds can be obtained, substituting Fe^{3+} cations. Powder and single crystals of a sodium–potassium β'' ferrite showing ferrimagnetic properties of chemical formula $(Na, K)_{1+x}Fe_{11-x}Zn_xO_{17}$ ($x \sim 0.9$) have been synthesized recently (*1*) by using bivalent Zn^{2+} cation in order to stabilize the structure. Single crystals have a platelet shape and crystallize in the rhombohedral $R\bar{3}m$ space group, hexagonal c axis lying perpendicularly to the platelet plane. According to magnetic measurements (*1, 2*) a weak ferromagnetic component is superimposed to an antiferromagnetic component in the β'' (Na, K) ferrite, the magnitude of this component depending on the exact chemical composition of the compound.

A series of new compounds derived from this β'' ferrite have been obtained by ion exchange in molten salts by either complete or partial substitution of Li^+, Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+} cations for large cations (Na^+, K^+) (*2–4*). In some cases these new ferrites have magnetic properties and crystal structure very different from the original β'' ferrite (*1, 2*). The case of the Li^+-exchanged β'' ferrite is particularly interesting, since after ionic exchange a spinel-like crystal with platelet shape is obtained. The present work has been undertaken in order to examine the crystal structure and magnetic properties of this new spinel phase.

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2. Experimental

A powder of β'' (Na, K) ferrite of nominal composition $Na_{1.3}K_{0.6}Fe_{10.1}Zn_{0.9}O_{17}$ has been used as starting material. Details about the synthesis is given elsewhere (*1*). The ionic exchange has been carried out in a molten salt of $LiNO_3$ at $T = 370°C$ for $t = 20$ hr. After exchange, the product was separated from the salt with boiled water and cleaned with distilled water.

The X-ray diffraction pattern shown in Fig. 3b can be indexed on the basis of cubic cell, with parameter $\langle a \rangle = 8.23(5)$ Å. Microcrystals of the exchange spinel are in platelet form; the crystal morphology is retained during the ionic exchange. The crystal size can vary from 0.1 to 0.3 mm.

Examination of a single crystal (extracted from this powder preparation) with the precession camera reveals that the space group is cubic primitive: $P4_132$, or its enantiomorph $P4_332$.

Differential thermal analysis measurements on exchanged powder spinel phase show a slow change in the slope of the ΔT curve, beginning at 650°C. This effect is probably due to an ordering phenomena on the octahedral sites as in the α-$LiFe_5O_8$ spinel case. In order to determine the exact chemical formula of the exchanged spinel and the distribution of Li, Zn, and Fe cations on all sites, we performed a structural refinement from single-crystal data.

3. Crystal Structure

The single crystal we studied was in platelet form of dimensions 0.20 mm × 0.25 mm × 0.09 mm and was extracted from the exchanged powder sample. Data collection has been performed by using a CAD4 four-circle diffractometer with Ag$K\alpha$ radiation. The cell parameters as revealed by centering of reflections are $a = b = c = 8.239(1)$ Å. All reflections from a $\frac{1}{2}$ sphere in ($3° < \vartheta < 30°$) range were measured with the ω-scan technique (scan with: $\Delta\omega = 1.4°$, speed $= 0.93°/\text{min}$). A total of 7903 reflections were measured; after averaging according to the 432 Laue Class, 478 independent reflections with $F > 3\sigma$ were retained. The structural refinement was carried out with Enraf–Nonius structure determination package—SDP (*5*); "*in situ*" absorption correction was performed. The weight attributed to each reflection during the refinement was $w = 1/\sigma^2(F_0)$ where $\sigma(F_0)$ was classically defined as in Ref. (*11*) (stability factor: 0.04). Diffusion factors of neutral atoms have been used. The starting atom parameters we used were those reported for the spinel α-$LiFe_5O_8$ (*6*).

In the case of a (Li, Zn) spinel structure the chemical formula can be written

$$\underset{A}{[Fe_{1-x}Zn_x]}\underset{B}{[Fe_{(3+x)/2}Li_{(1-x)/2}]}O_4,$$

where A stands for the tetrahedral sites of the spinel structure and B for the octahedral sites.

At the beginning of the refinement we had to determine:

(a) the Zn^{2+} location into the structure;

(b) the repartition of Li^+, Fe^{3+} cations on the octahedral sites of the structure; and

(c) the right space group ($P4_132$ or its enantiomorph $P4_332$).

At the early stages of refinement, we refined the atomic positions and the isotropic thermal parameters in the space group $P4_332$. Then we refined atom populations on the sites.

The refined population of the lithium and Fe^{3+} atoms are given in Table I; from the refined values of the population parameters we may conclude:

(1) The (*4b*) octahedral site is partially occupied by Fe^{3+} cations, while the refined population is much greater than the theoretical one.

(2) The (*8c*) tetrahedral site is probably

TABLE I

COMPARISONS BETWEEN THEORETICAL AND CALCULATED POPULATION PARAMETERS FOR THE Li, Fe ATOMS IN THE Li-EXCHANGED SPINEL COMPOUND

Atom	Position	Theor. population	Obs. population
Fe1	8*c*	1.0	1.038 (*6*)
Fe2	12*d*	1.0	0.894 (*6*)
Li	4*b*	1.0	5.21 (*2*)

occupied by Zn^{2+} cations. In the spinel-like structure the Zn^{2+} ions generally occupy tetrahedral positions; in addition, Zn^{2+} cations are located in the tetrahedral sites of the spinel blocks of the starting β'' (Na, K) ferrite as revealed from the single crystal's refinement (*2*). As a matter of fact, the refined value of population of the (8*c*) site is slightly greater than the theoretical one (see Table I).

(3) The (12*d*) octahedral site is partially occupied by lithium atoms. The refined population of this site is apparently too weak.

Following to that analysis, by comparing between the theoretical and refined population parameters the exact repartition of Li^+, Fe^{3+}, and Zn^{2+} atoms in the different sites was deduced. After fixing the occupation parameters, we refined both the atomic position and the isotropic thermal factors.

The final refined atomic positions are given in Table II. The introduction of anisotropic thermal parameters did not lead to better results (these ones could not be defined, probably because of the presence of domains, in the crystal, belonging to two enantiomorphic space groups ($P4_132$, $P4_332$). In the case of α-$LiFe_5O_8$ such domains have been evidenced by transmission electron microscopy (*7*).

TABLE II

FINAL POSITIONAL AND ISOTROPIC THERMAL PARAMETERS ($P4_332$ SPACE GROUP)

Atom	Posit.	Population	*x*	*y*	*z*	*B*(Å^2)
Fe1	8*c*	0.75	0.0	0.0	0.0	0.35(2)
Zn	8*c*	0.25	0.0	0.0	0.0	0.35(2)
Fe2	12*d*	0.90	$\frac{1}{8}$	0.3750(5)	$\frac{1}{4} - y$	0.42(2)
Li2	12*d*	0.10	$\frac{1}{8}$	0.3750(5)	$\frac{1}{4} - y$	0.42(2)
Fe3	4*b*	0.55	$\frac{5}{8}$	$\frac{5}{8}$	$\frac{5}{8}$	1.1(1)
Li3	4*b*	0.45	$\frac{5}{8}$	$\frac{5}{8}$	$\frac{5}{8}$	1.1(1)
O1	24*e*	1.0	0.1316(7)	0.1377(6)	0.8698(7)	0.26(4)
O2	8*c*	1.0	0.3737(7)	*x*	*x*	0.46(8)

Note. *wR* = 5.7%, *R* = 7.0%.

TABLE III

INTERATOMIC DISTANCES OF CATION COORDINATION POLYEDRA (Å)

Fe1 tetrahedron	
Fe1–O1	1.915(3) (×3)
Fe1–O2	1.818(2) (×1)
⟨Fe1–O⟩	1.890(3)
O1–O1	3.111(3) (×3)
O1–O2	3.063(6) (×3)
Fe2 octahedron	
Fe2–O1	1.971(3) (×2)
Fe2–O1	2.044(3) (×2)
Fe2–O2	2.078(2) (×2)
⟨Fe2–O⟩	2.031(3)
O2–O2	2.945(5) (×1)
O1–O1	2.861(6) (×5)
O1–O2	2.828(6) (×3)
O1–O2	2.908(6) (×3)
Fe3 octahedron	
Fe3–O1	2.044(3) (×6)
O1–O1	2.781(3) (×6)
O1–O1	2.996(6) (×6)

Therefore, the chemical composition is

$$[\underbrace{Fe_{2.7}Li_{0.3}}_{B_1},\ \underbrace{Fe_{0.55}Li_{0.45}}_{B_2}]\,[\underbrace{Fe_{1.5}Zn_{0.5}}_{A}]O_8,$$

where B_1, B_2 denote two octahedral sites and A denotes a tetrahedral site.

A structural refinement considering the $P4_132$ group did not give better results (the reliability factor at the end of the refinement was slightly higher in comparison to that shown in Table II). More significant interactomic distances, in the different polyedra of the structure, are shown in Table III.

On the other hand, we have calculated the effective valence of the different cations and

TABLE IV

CALCULATED VALENCES OF OCCUPIED SITES IN $Li_{0.75}Fe_{4.75}Zn_{0.5}O_8$

Sites	O(1)	O(2)	Cation valence
8*c* [Fe(1)]	(×1) (×3) 0.650	(×1) ×(1) 0.856	2.8
12*d* [Fe(2)]	(×1) (×2) 0.557 (×1) (×2) 0.459	(×3) (×2) 0.421	2.9
4*b* [Fe(3)]	(×1) (×6) 0.459		2.7
Oxygen valence	2.1	2.1	

Note. Multiplicities of coordination bonds (horizontaly and verticaly in the table) are indicated between brackets.

anions of the structure, on the basis of the Brown's model (*8*): $V_c = \Sigma_j S_{ij}$ and $V_a = \Sigma_i S_{ij}$, where $S_{ij} = (D_{ij}/R)^{-N}$; D_{ij} stands for the distance between *i* cation and *j* anion, *R* and *N* are constants depending on the cation. We have shown in Table IV the results of this calculation. The 0.4 Zn^{2+} cation by formula unit in the (8*c*) site is found from the calculated valence, in agreement with the refined population parameter. Calculated valences on the 12*d* and 4*b* sites, confirm the partial occupation of these sites by lithium, but the corresponding population parameters (0.15 and 0.15), are too small. This is not surprising, because it is well known that Brown's or Zachariasen's valence calculation methods do not give good results with alkali cations (*12*).

4. Magnetic Properties

Magnetization measurement have been performed at S.N.C.I. Laboratory in Grenoble, on exchanged spinel powder. The Curie temperature is T_c = 575(5)°C. Figure 1 allows to compare the magnetization curves at T = 4 K of a powder sample before and after annealing at 600°C during 24 hr; it is evident from Fig. 1 that, before annealing, magnetization saturation is not reached, even at magnetic field as high as 200 kOe. After annealing the magnetization curve tends to be more easily saturated; the value of the magnetization is about 80 emu/g; Fig. 1. Therefore, the magnetic properties depend strongly on the thermal treatment of the sample; however, in all cases the magnetization vector lies in the platellet plane, parallel to the (111) plane of the cubic cell. Figure 2 shows the variation of the coercive field with the crystal grain size; the higher

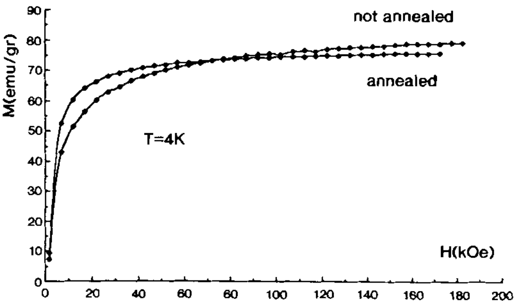

FIG. 1. Influence of annealing at the magnetization curve for a powder sample of (Li, Zn) exchanged compound.

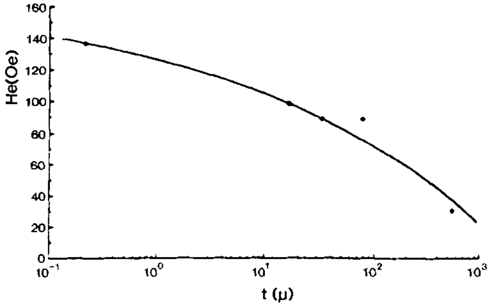

FIG. 2. Variation of coercive field with crystal grain size (*t*) for a spinel (Li, Zn) exchanged compound.

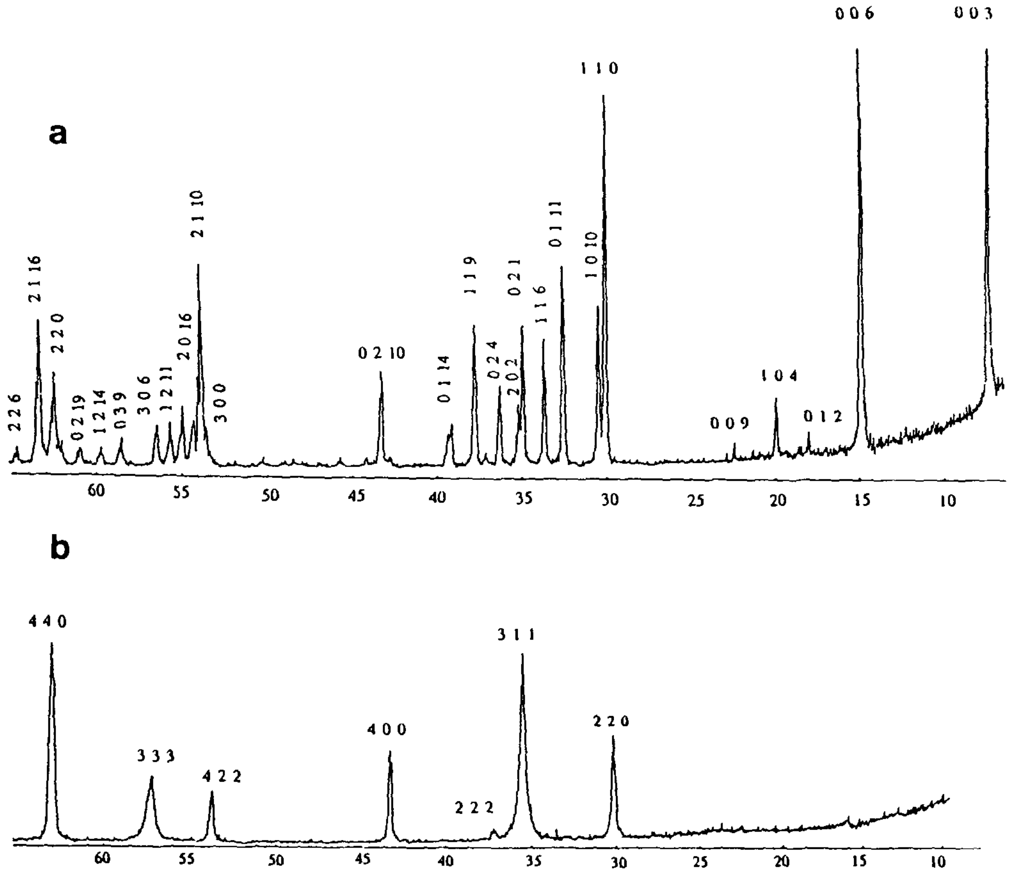

FIG. 3. X-ray diffraction pattern from (a) $Na_{1.3}K_{0.6}Fe_{10.1}Zn_{0.9}O_{17}$ starting material; (b) (Li, Zn)-exchanged spinel compound.

observed value is $Hc = 134$ Oe, with crystallites of 0.2 μm size.

5. Discussion

(*a*) *Structural Properties*

As revealed from electron microscopy studies (*1*, *9*) the conduction region of the original β'' ferrite disappear during the ionic exchange and the adjacent spinel blocks are joining after exchange; the [111] crystal axis of the obtained spinel is parallel to the previous hexagonal axis of the β'' ferrite structure.

The refined chemical unit formula of the compound is $Li_{0.75}Fe_{4.75}Zn_{0.5}O_8$. As the starting β'' (Na, K) ferrite powder had the nominal composition $Na_{1.3}K_{0.6}Fe_{10.1}Zn_{0.9}O_{17}$, we may note that before and after ionic exchange the amount of Zn^{+2} remains practically unaltered and positioned in the tetrahedral sites of the spinel structure.

The superstructure reflections with *h*, *k*, *l*, indices not having the same parity are not visible on the powder X-ray diffraction pattern. Nevertheless, they appear on the single crystal's diffraction patterns obtained with the precession camera. Many weak superstructure reflections have also been col-

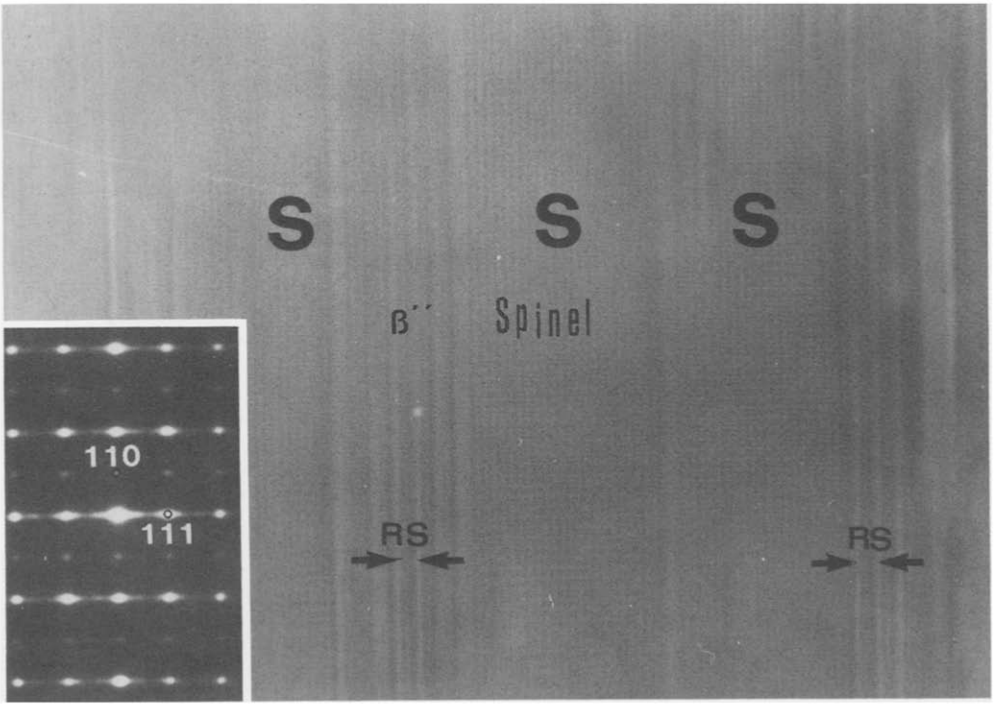

FIG. 4. Electron microscopy analysis of a large (Li, Zn) exchanged crystal; narrow β'' type domains are still present.

lected with the four circle diffractometer. A possible explanation is that in fact the order of the Fe^{3+}/Li^{+} cations on the octahedral sites of the exchanged spinel structure is incomplete, so the superstructure reflections do not appear on the powder diffraction pattern.

A significant broadening of the (333) reflections in the X-ray diagram of Fig. 3 reveal the presence of stacking defects. Also, X-ray diffraction patterns performed with the precession camera show the presence of streaks along the [111]* direction of the reciprocal lattice. These stacking defects tend to disappear after annealing at 600°C, as it is confirmed by X-ray diffraction.

(b) Magnetic Properties

In this spinel a relatively strong shape ansotropy exists which is responsible for the relatively important value of the measured coercive field; this field is much higher than α-$LiFe_5O_8$ ($Hc = 4$ Oe) prepared by direct synthesis methods (*10*).

On the other hand, stacking defects in this spinel structure are hindering domain wall displacements. After annealing, the defects disappear and the magnetization tends to be saturated at high fields. According to the chemical formula found by crystal structure refinement, the saturation magnetization, should be 113 emu/g at 0 K, considering a colinear ferrimagnetic arrangement. This value is higher than the observed one (about 80 emu/g at 4 K) on powder. The observed saturation magnetization using a large single crystal is yet much lower (about 60 emu/g).

A likely explanation is that, in reality, the exchange is not complete into large grains or crystals. Some small domains with the starting β'' ferrite structure, still unexchanged, could drastically reduce the magnetization of the sample. A study, by high-resolution electron microscopy, confirms the existence of such domains; see Fig. 4.

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