

Ion Distribution and Saturation Magnetization of Aluminum Substituted Lithium Ferrites

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Abstract - Ion distribution is determined in a series of aluminum substituted lithium ferrites by carefully analyzing the powder X-ray diffraction patterns. A new finding is that Al³⁺'s substitute the Fe³⁺'s in tetrahedral sites as well as in octahedral sites of the spinel structure. The proper formula, then, is (Fe³⁺_{1-a}Al³⁺_a)[Li⁺_{0.5}Fe³⁺_{1.5-(x-a)}Al³⁺_{x-a}]O₄, where *a* is approximately 0.23x²+0.22x. The saturation magnetizations are calculated and compared with the measured values.

I. INTRODUCTION

Lithium ferrites are technologically important as microwave latching device materials. They have high Curie temperature (*T_c*) for good thermal stability, high room temperature saturation magnetization ($\sigma_{s,300K}$), excellent squareness (*M_r/M_s*), and an economic price. However, the $\sigma_{s,300K}$ should be adjustable from 4 to 80 emu/g to be useful over a wide frequency range. This can be achieved, at least partially, by substituting such cations as Ti⁴⁺ and Al³⁺[1].

The materials have the inverse spinel structure. Unsubstituted pure lithium ferrite has the formula (Fe³⁺)[Li⁺_{0.5}Fe³⁺_{1.5}]O₄. The parentheses () and brackets [] indicate ions distributed on tetrahedral and octahedral sites, respectively. The magnetic spins of the two sites are antiparallel. It is believed that Al³⁺'s substitute Fe³⁺'s in the octahedral sites to give the formula (Fe³⁺)[Li⁺_{0.5}Fe³⁺_{1.5-x}Al³⁺_x]O₄[2]. If this is the case, x=0.5 material becomes antiferromagnetic. However, the room temperature saturation magnetization of the material is about 23emu/g [1,2].

The authors attempt to resolve the contradiction. A powder X-ray diffraction (XRD) analysis provides details of crystallographic information, especially the cation distribution. The saturation magnetization is calculated using the cation distribution. The result is compared with measured results.

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II. EXPERIMENTAL

Samples were prepared using 99.9% pure powders of Li₂CO₃, Fe₂O₃, and Al₂O₃. Predetermined quantities were mixed in a ball-mill, and heat treated 10 hours at 1000°C. Sample compositions were analyzed by atomic absorption spectroscopy for Li⁺, Al³⁺, Ti⁴⁺ and titration with K₂Cr₂O₇ for Fe³⁺, respectively. Product compositions are within 2% deviation from target compositions (Table I).

Powder diffraction patterns were obtained using a computer controlled diffractometer (Rigaku D/MAX 3-C). A graphite monochromator filtered the X-ray from the Cu tube (40kV, 40mA). The data were collected for 20 seconds at every 0.04° step. A single scan from 2θ=10° to 90° required more than 10 hours. The pattern was analyzed with a numerical method (section III).

The room temperature σ_s at 10 KOe was measured with a vibrating sample magnetometer (VSM, TOEI model 5). The Curie temperature was measured using a thermogravimetric analyzer (Perkin Elmer TGA7) with a ramping mode of 20°C/min. from 30°C to 700°C.

III. ION DISTRIBUTION

The Rietveld method[3] analyzes XRD profiles by simulation and nonlinear-least-square-fitting. The technique simulates a spectrum using a set of structure parameters, including ion distributions. The parameters are refined to minimize the difference between the simulated and the measured spectrum. A typical output is given in Fig. 1. Reliability factors ($R.I.=\sum[|I_{obs.}-I_{simul.}|]/\sum I_{obs.}$) of current results are within 0.02-0.05. (This value is small enough to be accepted

TABLE I

SAMPLE COMPOSITIONS		
x	target	analyzed
0	Li _{0.5} Fe _{2.5} O ₄	Li _{0.49} Fe _{2.51} O ₄
0.1	Li _{0.5} Fe _{2.4} Al _{0.1} O ₄	Li _{0.51} Fe _{2.38} Al _{0.11} O ₄
0.2	Li _{0.5} Fe _{2.3} Al _{0.2} O ₄	Li _{0.51} Fe _{2.29} Al _{0.20} O ₄
0.3	Li _{0.5} Fe _{2.2} Al _{0.3} O ₄	Li _{0.51} Fe _{2.19} Al _{0.30} O ₄
0.4	Li _{0.5} Fe _{2.1} Al _{0.4} O ₄	Li _{0.51} Fe _{2.10} Al _{0.39} O ₄
0.5	Li _{0.5} Fe _{2.0} Al _{0.5} O ₄	Li _{0.52} Fe _{1.98} Al _{0.50} O ₄

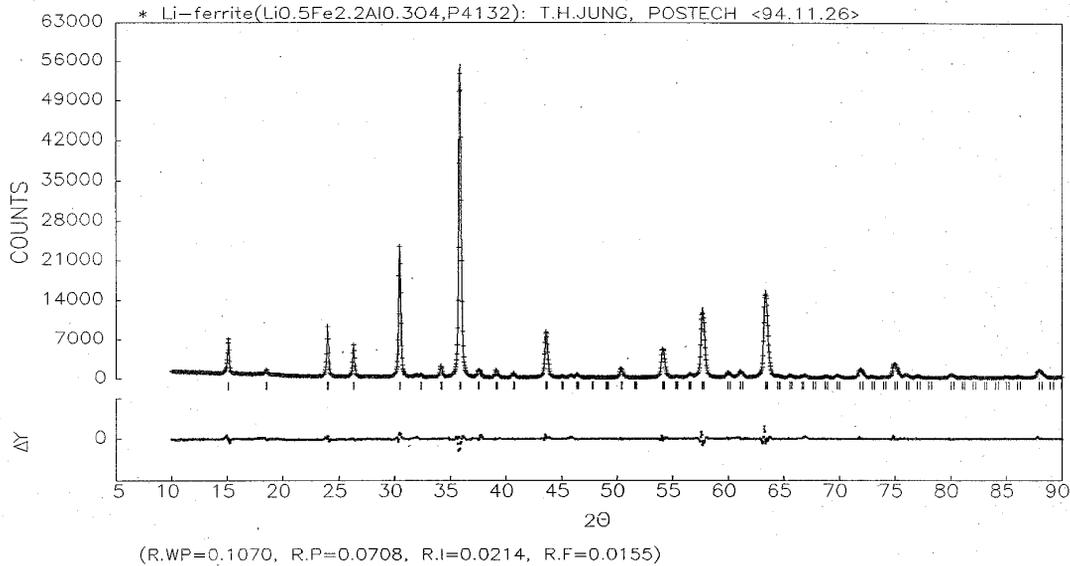
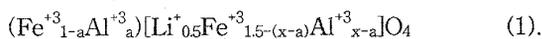


Figure 1. A typical output of the XRD analysis. Upper part displays the best-fit profile (line), superimposed on the measured data (cross). The difference is shown at the bottom. Tick marks, in the middle, indicate the Bragg angles for both CuK α_1 and CuK α_2 .

as a publishable analysis[4].) The error seems to be associated with XRD sample preparation and slight misalignment of the diffractometer, inspecting the details of mismatch of peak position and shape in the bottom profile of Fig. 1. No other phase than the lithium ferrite could be identified with such an intensive analysis.

Table II lists the refined ion distribution. (Standard deviations are 2.5-3% of the distributions depending on the ion and the composition.) The distribution is the same as the probability of finding "i" ion in "s" site ($p_{i,s}$). Note that Al $^{3+}$ distribution over the tetrahedral sites is appreciable. This demonstrates that the previous knowledge on the Al $^{3+}$ distribution[2] is not correct. Then the proper formula is



The subscript in (1) is the number of "i" ions in "s" sites ($n_{i,s}$). In the tetrahedral sites, $p_{i,tet} = n_{i,tet}$. In the octahedral sites, however, the probability is one half of the number, i.e., $p_{i,oct} = n_{i,oct}/2$. An example is $p_{Li,oct}=0.25$, and $n_{Li,oct}=0.5$.

The total number of aluminum ions in a molecule, $p_{Al,tet}+2p_{Al,oct}$, is different from "x" by 10%. They can be made the same, if a linear constraint is imposed on the Rietveld analysis. Such a treatment, however, will not improve the significance of the result. The number of aluminum in the tetrahedral site can be approximated as follows :

$$n_{Al,tet} = a \approx 0.23x^2 + 0.22x \quad (2).$$

IV. SATURATION MAGNETIZATION

The σ_s of a molecule is calculated by (3), using the ferrimagnetic spin configuration.

$$\sigma_s = (n_{Fe,oct} - n_{Fe,tet}) \cdot 5 \text{ Bohr magneton}(\mu_B) \quad (3),$$

where $n_{Fe,oct}=2p_{Fe,oct}$, and $n_{Fe,tet}=p_{Fe,tet}$. It is compared with the measured values and literature values[1,5], in Table II and Fig. 2. Difference between the calculated magnetization and the measured value increases as the amount of aluminum(x) increases.

Such a trend should be understood by thermal variation of magnetization (i.e., σ/σ_s vs. T/T_c).

TABLE II
ION DISTRIBUTION AND MAGNETIC PROPERTIES

X	ion distribution						σ_s (emu/g)			T_c (K)	
	tetrahedral		octahedral				meas.	calc.	rep't	meas.	rep't
	Fe $^{+3}$	Al $^{+3}$	Li $^{+}$	Fe $^{+3}$	Al $^{+3}$						
0	1.00	-	0.25	0.75	-	60.9	71.6	61.6*	924	903*	
0.1	0.97	0.03	0.25	0.72	0.03	54.2	63.9	52.9**	912	-	
0.2	0.95	0.05	0.25	0.68	0.07	48.5	56.8	-	897	856*	
0.3	0.91	0.09	0.25	0.65	0.10	43.3	55.0	41.3*	892	-	
0.4	0.88	0.12	0.25	0.62	0.13	38.9	50.7	30.0*	885	781*	
0.5	0.83	0.17	0.25	0.60	0.15	35.5	51.6	22.5*	873	-	

* read from Fig. 1 in ref. [1], ** ref. [5]

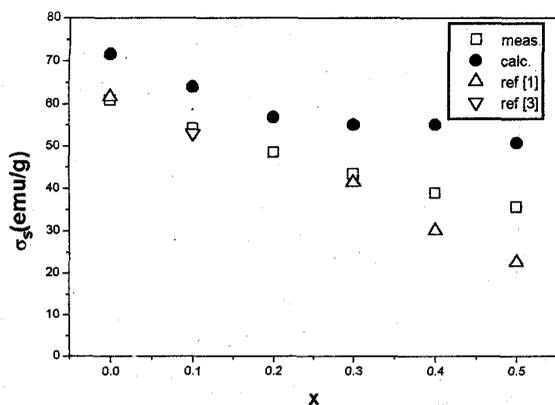


Figure 2. Comparison of measured magnetizations ($H = 1$ Tesla) at room temperature and calculated values for complete spin alignment from ion distribution

The measured magnetization represents thermally disturbed spin state at room temperature, whereas, (3) assumes complete spin alignment at 0K. For a ferrimagnetic materials, there is not a simple equation for the variation, though coupled Brillouin equations describe the behaviour of sublattices. On the other hand, single expression (4) describes the overall behaviour of a ferromagnetic material[6].

$$\frac{\sigma}{\sigma_s} = \tanh \left(\frac{\sigma/\sigma_s}{(T/T_c)} \right) \quad (4)$$

where σ_s is the net magnetization at 0K, T_c is the Curie temperature. Generally, σ/σ_s drops much faster in a ferrimagnetic materials than described by (4) for a ferromagnetic materials, as T/T_c increases[6]. The same is true in current system, where σ/σ_s drops from 0.85 to 0.69 as T/T_c increases from 0.323 (at $x=0$) to 0.341 (at $x=0.5$).

The saturation magnetization can be estimated, by introducing (2) to (3), as follows :

$$\sigma_s \approx 2.5 - 2.8x + 2.3x^2 \text{ Bohr magneton}(\mu_B) \quad (5)$$

Equation (5) enables us to estimate either the saturation magnetization or the aluminum content, once one of them has been designed.

The current result firstly justifies the non-zero net magnetic moment of the $x=0.5$ material. However, the ion distribution should be improved by a complementary study, such as Mossbauer spectroscopy.

V. CONCLUSIONS

$(\text{Fe}^{+3}_{1-a}\text{Al}^{+3}_a)(\text{Li}^{+}_{0.5}\text{Fe}^{+3}_{1.5-(x-a)}\text{Al}^{+3}_{x-a})\text{O}_4$ is the proper formula of aluminum substituted lithium ferrites, where a approximates $0.23x^2 + 0.22x$. The net magnetic moment is calculated by using the refined ion distribution. The non-zero net magnetic moment of the $x=0.5$ material is justified.

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