THE INFLUENCE OF COPPER CONCENTRATION ON MAGNETIC PROPERTIES OF SOME NANOCRYSTALLINE $Li_XCu_{1-2X}Fe_{2+X}O_4$ FERRITES

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The stoichiometric $Li_xCu_{1-2x}Fe_{2+x}O_4$ samples with spinel structure were obtained by standard ceramic technology and milled several hundred hours in air or liquid environment. The average size of the particles was determined by means of X-ray diffraction. The structure and magnetic properties were investigated. The magnetization, coercive field and lattice constant are changing vs milling time and chemical composition. The coercive filed increases from 3 Oe to 120 Oe, for $Li_{0.5}Fe_{2.5}O_4$ sample milled 238 hours, while the specific magnetization and the lattice constant decrease vs. milling time.

1. Introduction

The stoichiometric Li-Cu ferrites exhibit cubic structure (Fd3m) at temperatures higher than 800°C [1]. The increase of Cu content and the decrease of the treatment temperature lead to a decrease of the lattice symmetry. $Li_{0.5}Fe_{2.2}O_4$ – $LiMn_2O_4$ solid solutions were investigated by X-ray powder diffraction and infrared spectroscopy [2]. By increase of the Fe^{3+} ions concentration results in a better ordering of Li^+ cations on the octahedral sites. In the disordered form, Li^+ cations occupy the 16d positions in the cfc cell (Fd3m), while in the ordered form these cations occupy 4b and 12d sites in the cubic primitive cell (P4$_1$34). For a large content of Mn, $(1-x)Li_{0.5}Fe_{2.2}O_4*xLiMn_2O_4$ samples became tetragonally distorted and Li^+ can occupy the tetrahedral sites [3,4].

The diminishing of the average particles size is associated with the modification of structure and magnetic properties [5]. $ZnFe_2O_4$ nanocrystalline particles obtained by high-energy ball milling technique exhibit a change from antiferromagnetic to ferromagnetic behavior, which is explained by an increase of the strength of the magnetic interactions between the magnetic clusters with the decrease of the average size of the particles.

Our aim is to reveal the structural and magnetic changes induced in $Li_{0.5x}Cu_{1-x}Fe_{2+0.5x}O_4$ samples by high-energy ball milling.

2. Experimental

Li_2O-CuO-Fe_2O_3 samples were sintered at temperatures of about 900°C and milled for different times. The structure was determined by means of X-ray analysis, which confirmed the presence of only the spinel phase. The magnetic properties were investigated by using a Foner type magnetometer and a vibrating sample magnetometer (VSM) in the temperature range 77-900 K. The Curie temperatures were determined from the plotted dependence:

$$\sigma^2 = a\,(T_C - T) \tag{1}$$

The phases composition, the lattice constants, the average size of the mosaic blocks, and the induced microstrains were determined by using a DRON diffractometer [6]. The cation distribution was determined by using the known relation for relative intensities:

$$I_r = kmPL\left|F_{hkl}\right|^2 \exp(-2B(\frac{\sin\theta}{\lambda})^2) \tag{2}$$

A polycrystalline Si sample was used as standard for the half-width instrumental correction and for sample displacement correction. The samples were prepared by milling in an agate mill in different controlled atmospheres (water, alcohol).

3. Results and discussions

The phase composition of the samples remains practically unchanged, but the half-width of the maximum observed in X-ray diffraction patterns increases by increasing the milling time. The bulk samples have a monotonous decrease of the M_s vs. temperature and Cu concentration [6]. The lattice constant of the Cu stoechiometric ferrite exhibit a maximum, which is function of the milling time, while the Li ferrite presents a decrease of the lattice constant vs. milling time. (see Tables 1 and 2). The diminishing of the value of the lattice constant and of the relative intensities for Li-ferrites (see Table 1) could be associated with a transition to a lower symmetry state and/or a migration of the Li^+ to the crystallite boundaries. The redistribution of the cations associated with a transition from the disordered F3dm to the ordered $P4_134$ structure takes places by increasing the milling time. The increase of the lattice constant of the Cu ferrite vs. milling time could be associated with an increase of Cu and/or Fe cations concentrations in a low valence state (see Table 2).

Table 1. The variation of the diffraction peaks vs. milling time for $Li_{0.5}Fe_{2.5}O_4$ ferrite.

Milling time	(HKL)					a (Å)
(h)	(220)	(400)	(422)	(333) (511)	(440)	
114	24.9	27.8	11.9	28.8	46.3	8.351
238	26.2	19.0	10.7	27.2	47.4	8.335
337	32.6	23.9	21.8	32.1	57.5	8.311

Table 2. The variation of the diffraction peaks vs. milling time for $CuFe_2O_4$ ferrite.

Milling time	(HKL)			a (Å)
(h)	(220)	(400)	(440)	
42	21.9	21.9	17.1	8.359
91	-	-	24.7	8.397
139	19.9	15.5	28.7	8.392
212	20.0	0	27.3	8.382

The powder resulted from the milling process is formed by small single particles. The magnetic measurements made on the milled samples indicate an increase of the coercive field from less then 3 Oe for $Li_{0.5}Fe_{2.5}O_4$ bulk samples to about 120 Oe for the 238 hours milled sample. For the samples sintered in the same conditions it can be observed an increase of the magnetization and of the coercive field vs. the copper content.

The coercive field strongly depends on the Cu content in the sample and of the microstrains level. We observed also a decrease of the specific magnetization and coercive field vs. milling time (see Fig. 1). It could be assumed that the particles are formed from an ordered core and a disordered surface layer.
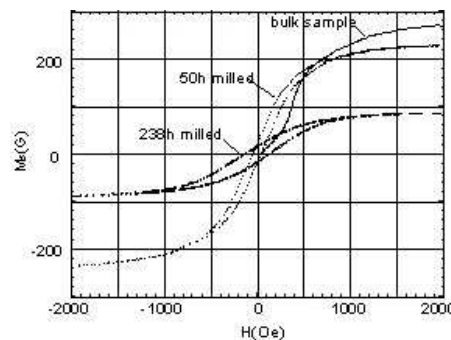

Fig. 1. The hysteresis curves of the milled $Li_{0.5}Fe_{2.5}O_4$ ferrite.

A small increase of the coercitive field is observed when the Co content increases (see Fig. 2). The magnetization also increases with the Cu concentration increase. The magnetic moment increases due to the contribution of the Cu cations.

The minimum observed size of about 6 nm was obtained relative quickly after milling in alcohol (about 50 hours), while the samples milled in air became nanosized after about 100 hours. The milling time, which is needed to obtain the minimum size, was very short comparatively with other ferrites [1]. The samples preserved their cubic structure, despite of the prolonged milling time. The powder consists of single-domain particles. The atomic magnetic moments are aligned parallel or antiparallel with respect to the easy direction of magnetization in the inner part of the particle. In the boundary layer the magnetic moments could be disordered concerning the magnetic moment of the particle due to the absence of the Fe - O bond.
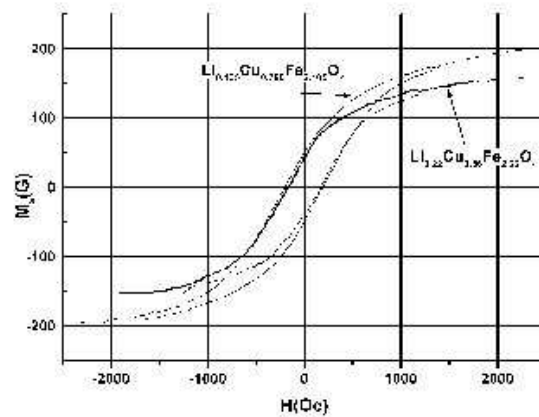

Fig. 2. The hysteresis curves of the 50 hours milled $Li_{0.22}Cu_{0.56}Fe_{2.22}O_4$ and
$Li_{0.105}Cu_{0.79}Fe_{2.105}O_4$ ferrites.

A model concerning the reduced coordination and the surface anisotropy in ionic materials was developed by Kodama et al [7] in the hypothesis that the exchange interactions have the same magnitude for bulk and surface atoms, but the exchange energy is less for the surface atoms due to their lower coordination. The surface anisotropy of the quasi-spherical particles can be considered locally, uniaxial and radial oriented. In the absence of the external field, the effect of the radial surface anisotropy is the obtaining of a null magnetic moment for the boundary layer. If an external field is applied, the magnetic moment of the boundary layer is oriented parallel with its direction. Concerning ionic compounds the localized magnetic moments do not change as magnitude near the surface, but the orientation of each moment could be altered, due to the competing super-exchange interactions in the incomplete coordination shell from the surface or near the surface ions. This leads to a disordered spin configuration and a decrease of the average net moment as compared to bulk materials.

The magnetic measurements, performed at room temperature, indicate an increase of the coercitivity during the milling. The milled samples have a coercitivity of about 40 times higher than those of the bulk samples and a remanence, which represents one third of the saturation magnetization.

The magnetic measurements at low temperatures indicate a superparamagnetic behaviour of the samples. Recent research on ferrites nanoparticles shows that, in the case of a small single-domain (nano-) particle a large variety of spin distribution it is possible, due to the "surface spin states". With the increase of the milling time an increase of the defect concentrations appears. The increase of the microstrains is quicker in comparison with the diminishing of the average size of the particles. When a threshold has been attained, a sudden decrease of the average size of the particles, followed by a microstrains relaxation appears (see Tables 3 and 4).

If we consider the cation distribution as:

$$(Li_\lambda Fe_{1-\lambda})_A[Li_{0.5-\lambda}Fe_{1.5+\lambda}]_B O_4 \qquad (3)$$

the intensity of (220) maximum relative to (311) maximum is given by the relation:

$$I_{r(220)} = 0.479 - 0.782 * \lambda \qquad (4)$$

Table 3. The variation of the lattice constant (a), average size of the mosaic blocks ($<\varepsilon^2>^{0.5}$), micro-distorsion ($\Delta a/a$) and of the cation distribution parameter (λ) vs. milling time for $Li_{0.5}Fe_{2.5}O_4$ samples.

Milling time (h)	a (nm)	$<\varepsilon^2>^{0.5}$ (nm)	$\Delta a/a$ (10^{-3})	λ
114	0.8351	11.0	0.923	0.18_3
238	0.8335	24.0	2.117	0.20_0
337	0.8331	6.2	0.000	0.17_1

Table 4. The variation of the lattice constant (a), average size of the mosaic blocks ($<\varepsilon^2>^{0.5}$), microdistorsion ($\Delta a/a$) and of the cation distribution parameter (λ) vs. milling time for $CuFe_2O_4$ samples.

Milling time (h)	a (nm)	$<\varepsilon^2>^{0.5}$ (nm)	$\Delta a/a$ (10^{-3})	λ
42	0.8360	> 2000	4.331	0.24_5
91	0.8397	6.0	1.408	0.27_1
139	0.8392	5.5	1.066	0.26_1
212	0.8382	5.8	1.742	0.26_0

A similar formula was obtained for $CuFe_2O_4$, in the assumption that that the copper cations occupy the tetrahedral and octahedral sites. The Li concentration on the A sites increases with the decrease of the average size of the particles (see Table 3), while the distribution parameter for $CuFe_2O_4$ ferrite remains practically unchanged (Table 4). The Fe cations concentration on B sites increases also with the decrease of the particles size, leading consequently to a decrease of the magnetic moment per molecule. This behavior could explain the diminishing of the specific magnetization. The magnetization curve of milled nanoparticles presents a maximum at low temperatures. The saturation magnetization decreases with the particle size increases (see Fig. 1). This dependence could be explained by: (i) the increase of the ratio between the volume of the inner core and the total volume of the particle or/and (ii) the modification of the cation distribution with the diminishing of the average size of the particles. In the boundary layer, the Li^+ cations occupy both the octahedral and tetrahedral sites. We expect a superparamagnetic behavior of our samples at low temperatures, but from the preliminary magnetic measurements only a decrease of the magnetization could be observed at temperatures lower than 150 K. This feature is typical for a frustrated magnetic system, like spin glasses systems.

4. Conclusions

The milled $Li_{0.5x}Cu_{1-x}Fe_{2+0.5x}O_4$ samples exhibit larger coercitive fields in comparison with bulk samples. This increase of the coercive field seems to depend more on the milling time than on the cation concentration. The magnetization depends on both the chemical composition and the milling time. The cations with a higher radius tend to migrate to crystallite boundaries, and Cu^+ and Fe^{2+} concentrations increase vs. milling time.

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