Structural and Magnetic Properties of Copper Substituted Mg-Ferrites

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Abstract. Polycrystalline ferrite powders of MgₓCuₓFe₂O₄ (x = 0.2, 0.4, 0.6, 0.8, 1) system synthesized by ceramic technology have been investigated. Samples showed the non-monotonic dependency of heat generation effect in AC magnetic field with increasing concentration of copper. To reveal peculiarities of the structural and magnetic state of the samples and their influence on the heat generation ability we performed a complex study, including X-ray diffractometry, Mössbauer spectroscopy, Scanning electron microscopy, measurements of temperature dependencies of susceptibility and saturation magnetization, hysteresis parameters and FORC.

Typical ferrimagnetic character with small coercivity and saturation magnetization was found. We carried out that anomalous influence of Cu²⁺ ion substitution respectively to the Mgₓ⁻CuₓFe₂O₄ ferrite powder manifested in heat generation ability rise up to x = 0.6. The subsequent sharp reducing of this characteristic were accompanied by the main phase crystal structure distortion followed by phase separation to cubic and tetragonal structure. This was matched by an increase of ferrite particles crystallite size and size distribution appearance. The saturation magnetization and Curie temperature dependencies observed for powders via Cu substitution was explained by phase composition, the cations distributions between ferrite sublattices, modulation of exchange interaction.

1 Introduction

The new opening opportunities for ferrite’s applications in different fields of modern industry (catalysis, adsorption, humidity sensors, ferrofluids and ferroelastomers technology, components of health monitoring systems and medicine) require the involvement of modern and powerful experimental techniques. The properties-structure-sizes interdependence study allows to manage ferrite’s functionality [1-3]. Among a number of industrial important ferrite compositions magnesium ferrite (MgFe₂O₄) particles have favorable magnetic properties and biological compatibility. It is worth mentioning that MgFe₂O₄ particles of micrometer-range sizes are reported to exhibit greater magnetic heating than do other ferrites [4-5], but a lot of afforts have veen made to investigate of the best composition of ferrite particles to obtain effective heating abilities under application of alternating magnetic field remains controversial [6-7]. The investigation of the different effects influence on the properties of ferrites, which are used as components of complex composite systems for the purposes of therapeutic implants, seems to be important.

It is known, that ferrites have the general formula (M₁₋ₓFeₓ)(M₁₋ₓFeₓ−zCzx)O₄. The divalent metal atoms M (Mg, Fe, Cu or mixture of them) can occupy either eight tetrahedral (A) or sixteen octahedral (B) sites of a cubic mineral spinel structure as depicted by the parentheses or brackets, respectively, z represents the degree of inversion. The complexity of the above formula and the nature of preparation techniques strongly suggest a variation in unit cell composition and possibly a variation in the arrangement of Mg²⁺ and Fe³⁺ ions over the available tetrahedral and octahedral sites. Depending on the cations distribution in (A) and (B) sites, two extreme states—normal (z = 0) and inverse (z = 1) or an intermediate mixed state may be realized. Ultimate magnesium ferrite (MgFe₂O₄) is an inverse spinel taken to be collinear ferrimagnetic [8,9], whose degree of inversion depends on the synthesis temperature and cooling rate [8,10]. The ultimate copper ferrite (CuFe₂O₄) exists in tetragonal and cubic structures [10]. The distortions from one structure to another is directly related to the magnetic properties. The cubic structure possesses a larger magnetic moment than that of the tetragonal one, because there are more cupric ions (Cu²⁺) at tetrahedral sites in cubic structure as compared to that in the case of tetragonal structure. As the ionic radii of the Fe, Mg and Cu cations (the ionic radius of Cu²⁺ (0.85...
difference minimization applying HighScore software.

PIXcel3D detector (Bragg-Brentano geometry, CuKα) referenced to performed with UnivemMS software. All spectra were measured using Curie balance (Ltd “Orion”) in (370kHz, 1.50kA/m) magnetic field was measured on laboratory equipment with IR-thermometer [7].

magnetic field 200 A/m and frequency ~1000 Hz, of saturation magnetization and susceptibilities were measured on Cappabridge MFK-1FA (AGICO) in magnetic field of 4,5 kOe, and Cappabridge MFK-1FA (AGICO) in magnetometer (LakeShore), temperature dependencies of magnetic susceptibility for the concentration dependencies of hyperfine magnetic field’s distribution. Mössbauer spectra of MgFe2O₄ is known to have an asymmetric structure is more effective than vice versa. As a spin-density transfer from (A) to the Fe [9] the supertransfer mechanism [9]. According to [11] the consequence, the (A) -site lines usually do not show any broadening of the subspectra due to [4] subspectra, and [4] B] sites.

3 Results and discussion

Plot of the temperature enhancement from room temperature (ΔT) for powders in the AC (370kHz, 1.50kA/m) magnetic field (Fig.1, a) shows that heat generation ability was improved with increasing the Cu substitution, the highest heat generation ability (ΔT ≈ 37°) was obtained at x = 0.6. Then, the heat generation ability abruptly decreases and lost over x = 1.0. Similar nonmonotoneous dependencies were observed for other ferrite compositions synthesized by the same technology and had different degree of heat generation. In order to gain more information regarding the structure and properties correlations in our synthesized Mg₁₋ₓCuₓFe₂O₄ powders we have undertaken X-ray diffraction, Mössbauer spectroscopy and complex magnetic properties study. 

The X-ray diffraction patterns of Mg₁₋ₓCuₓFe₂O₄ ferrite system for x = 0-1.0 (samples 1-6) analysis revealed the polycrystalline structure with μm-sized crystallites. The main phase in all samples is fcc (cubic) spinel. Several additional impurities of crystalline phases (MgO, Fe₂O₃, CuFeO₃) were identified as a reaction by-products. For the ultimate Cu-substitution (x = 1) the appearing of tetragonal ferrite structure in a very small amount have been determined. Lattice parameter of the cubic phase increases with Cu²⁺ content with small distortion from the linear dependence at x = 0.4-0.6 (Fig.1, a). The dependence of the integrated intensity ratio I(220)/I(222) on the Cu content revealed that there is a cations redistribution between (A) and [B] sites. 

Fig.2 shows the concentration variation of Mössbauer spectra, measured at 300K. The spectra indicate a magnetic ordering with spectral lines broadening via Cu-substitution. Mössbauer spectra analysis allowed to resolve at first exact phase composition: Fe₂O₃, CuFeO₃, Cu(Fe) phases additionally to the main spinel phase have been determined for x = 0 and x = 1, correspondingly. Then, spectra profile fitting in a simple model resolving (A) and [B] subspectra due to iron atoms in the two sublattices was applied. Mössbauer spectrum of MgFe₂O₄ is known to have an asymmetric broadening of the [B]-site lines indicating the presence of several subpatterns arising from the different possible nearest-neighbor (A)-site configurations via supertransfer mechanism [9]. According to [11] the more covalent character of the Fe(A) –O bond compared to the Fe(B) –O bond explains qualitatively why the spin-density transfer from (A) to [B] in the spinel structure is more effective than vice versa. As a consequence, the (A)-site lines usually do not show any structure that indicates the presence of a narrower hyperfine field’s distribution. Mössbauer spectra parameters resolved from fitting allowed to determine the concentration dependencies of hyperfine magnetic fields on Fe³⁺ atoms in different sublattices so as an inversion degree (z) changes.

ΔT = 1.0. Similar
x = 0-1.0. Similar
ABCD

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The degree of inversion was calculated from the subspectral areas \( \frac{I(A)}{I(B)} = \frac{f(A)}{f(B)} \cdot \frac{z}{2-z} \), assuming that the ratio of the recoilless fractions is \( \frac{f(B)}{f(A)} = 0.94 \) at room temperature. The resulting composition dependence of inversion degree plotted on Fig.3 demonstrates the changes at \( x=0.4-0.6 \).

Fig.2 (right panel) shows the temperature dependence of susceptibility \( \chi(T) \) for samples. The results exhibit normal ferrimagnetic behavior. The pure sample corresponds to \( x=0.2-0.8 \) and in accordance with XRD and Mossbauer phase analysis data. The ultimate ferrite sample with \( x=1 \) demonstrated multiphase behavior. The Curie temperature \( (T_c) \) obtained from susceptibility data is shown in Fig.3.

The Curie temperature \( (T_c) \) of the main phase in the ferrite samples measured from \( \chi(T) \) curves has nonmonotonic dependence via Cu substitution: gradual decrease of the \( T_c \) value to the sample with \( x=0.4 \) and followed by an \( T_c \) increase. It is known that \( T_c \) is determined by the overall strength of the intersublattice AB interactions, but sometimes the intrasublattice AA and BB interactions may become important. The decrease in \( T_c \) with increasing concentration of Cu may be explained by the modification of A-B exchange interaction strength due to the change of cations distribution between A and B sites.

Hysteresis loops \( J(H) \) for \( Mg_{1-x}Cu_xFe_2O_4 \) ferrite samples (Fig.4) showed nonmonotonic dependence: it is divided into three groups: I (\( x=0-0.2 \), curves 1,2); II (\( x=0.8-1 \), curves 5,6); III (\( x=0.4-0.6 \), curves 3,4). Similar non-monotonic behavior of hysteresis loops has been reported in several works subjected to study of substitution influence [12]. Magnetic parameters determined from the curves were analysed and plotted in as a Day’s diagram [13-14] \( (J_{rs}/J_s \text{ vs } H_c/H_c) \) (Fig.5, a). This diagram clearly demonstrated the three ranges that correspond to different sizes or domain state in the particles: I - the smallest particles are probably a mixture of SD (single domain) and PSD (pseudo single domain) particles, II - larger particles are mixture PSD and MD (multi domain) particles, III - the largest particles (multi-domain state of ferrite powders).

Fig.2. Mossbauer spectra at 300 K (left panel) and temperature dependence of susceptibility (right panel) in dependence on Cu substitution (correspondingly)
ranges are shown on (Fig 5 b, c, d). FORC was able to
detect the coercive force distribution as well as the
magnetic interactions within particles assemblage [15].

FORC diagrams were measured by saturating a
sample in VSM magnetometer in a field $H_{sat}$, decreasing
the field to a reversal field $H_{a}$, then sweeping the field
back to $H_{sat}$ in a series of regular field steps $H_{b}$ as
illustrated in color on Fig. 5 (b,c,d). This process is
repeated for many values of $H_{a}$ yielding a series of
FORCs, and the measured magnetization at each step as
the function of $H_{a}$ and $H_{b}$ gives $J(H_{a}, H_{b})$. The FORC
distribution $\rho(H_{a}, H_{b})$ is defined as the mixed second
derivative of the interaction surface.

For each sample we determined the main FORC
peak, which is the coercivity field corresponding to the
maximum of the FORC distribution (plotted on Fig. 5 as
$H_{c}=\frac{(H_{a}+H_{b})}{2}$, $H=(H_{b}-H_{a})/2$). The interaction field is
quantified with the full width at half-maximum of the
main peak of the FORC distribution parallel to the
abscissa axis through the maxima peak $H$. It was
revealed from FORC diagram that for $x=0.4-0.6$ large
multidomain particles were synthesized; the smallest
particles sizes corresponds to $x=0-0.2$ ; intermediate for
$x=0.8-1$. This fact was confirmed by SEM imaging
(Fig. 6, a,b,c) of particles with restoration of particles
sizes distribution (Fig. 6, d) where they measured from a
few to several tens of microns. Cu substitution tends to
increase particles sizes.

The decrease of $H_{c}$ is in accordance with the
increase of average particle’s size and the immoderate
nonmagnetic ions entering into the lattice that may result
in the energy reduction of magneto-crystalline
anisotropy that leads to the resulting heat generation
ability.

Summary

Synthesized by ceramic technology at 1473 K
polycrystalline Mg$_{1-x}$Cu$_x$Fe$_2$O$_4$ ferrite powders were investigated by structural and magnetic methods. The
effect of Cu-substitution ($x=0$, 0.2, 0.4, 0.6, 0.8, 1) was
investigated. To sum up the results we found that:
1)Synthesized ferrites demonstrated anomalous
heating ability via Cu substitution that is connected with
their structural and magnetic properties variation.
2) All samples demonstrated soft magnetic behaviour
with coercivity depending on particles sizes and domain
state.
3) Magnetic hyperfine interaction measured by
Mossbauer spectrometry showed that Cu$^{2+}$ has an
appreciable effect on the magnetic field of the octahedral
sites.
4) It was determined that magnetic properties of
synthesized ferrites are in accordance with particles sizes
and cations distribution.

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