Structural phase stability, magnetism and microwave properties of Co_2FeO_4 spinel oxide

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Abstract

Correlation between crystal structure and physical properties for Co_2FeO_4 spinel oxide are studied. There are two coexisting phases, Fe rich and Co rich spinels, for S80, S86, S100 samples. The S90 and S95 samples showed single phase nature. A small signature of second phase is noted for S95 sample from the temperature dependence of magnetization measurement. The single phase with single Curie temperature at about 453 K is confirmed for S90 sample. Interestingly, S95 sample showed minimum magnetic energy loss. The complex magnetic permittivity and dielectric permeability at 4.6 GHz and 7.2 GHz has been measured for all samples. There is a correlation between annealing temperature for the samples and measured electromagnetic properties.

1. Introduction

Formula of spinel ferrites is AB_2O_4. Most of them form cubic spinel structure with oxygen anions in fcc positions and cations in the tetrahedral and octahedral coordinated interstitial lattice sites, forming the A and B sublattices [1]. Depending on the distribution of magnetic cations among A and B sublattices and nature of superexchange interactions (J(A-O-B), J(B-O-B) and J(A-O-A)), spinel ferrites exhibited properties of different type magnets, like: ferrimagnet, antiferromagnet and paramagnet. A typical example is Fe_3O_4 (magnetite) and its derived compounds ($Fe_{3-x}M_xO_4$: M stands for Co, Mn, Zn, etc.) [2, 3]. $Fe_{3-x}Co_xO_4$ is attractive due to typical anisotropy character of Co ions. Most of the studies [4-6] are limited to the Fe rich regions ($x \leq 1$) of $Fe_{3-x}Co_xO_4$ series, although Co rich ($x \geq 2$) compounds have shown potential applications and interesting properties. For example, Co_3O_4 is an antiferromagnet (T_N~30 K) but its derivatives $Co_{3-x}M_xO_4$ [M = Al, Mn, Fe] [7, 8] have shown the diversity in magnetic properties (ferrimagnet and spin glass) and magneto-transport phenomena.

The present work focuses on the mechanical alloyed Co_2FeO_4 nanoparticles. The distribution of cations in Co_2FeO_4 $[(Co^{2+}_{1-x}Fe^{3+}_{x})_A[Co^{2+}_{x}Fe^{3+}_{1-x}Co^{3+}]_BO_4$, $0.18 \leq x \geq 0.45]$ is highly sensitive on the preparation techniques, as described in Ref.[9]. The presence of multi valence cations in B sublattice may attribute to a good magnetic semiconductor property in Co_2FeO_4. Hence, detailed information of the correlation between crystal structure and physical properties are very much essential. The study of electromagnetic properties in microwave and millimetre wave frequency range and their correlation with structural properties can give new information about polarization and relaxation processes in electrical and magnetic subsystems.

II. EXPERIMENTAL

Details of the material preparation are given in [9]. The stoichiometric amounts of high purity (>99.5) Fe_2O_3 and Co_3O_4 were mixed to obtain the compound Co_2FeO_4 spinel oxide. The mixture was ground using mortar and pestle for 2 hours. The mixed powder was mechanical alloyed in atmospheric conditions using Fritsch Planetary Micro Mill "P-7". After 100 hours milling, the alloyed powder was made into pellets of several batches. Each pellet was annealed at different temperatures in the range 700^{0}C to 1000^{0}C. The annealed samples have been denoted as SX, where X = 80, 86, 90, 95 and 100 for annealing temperature at 800^{0}C (6 hours), 860^{0}C (12 hours), 900^{0}C (12 hours), 950^{0}C (12 hours) and 1000^{0}C (3 hours), respectively. For annealing time 3 hours to 12 hours, there is no significant change in the room temperature X-ray diffraction (XRD) spectrum of the samples.

The main objective of this work is to study possible correlation between crystal structure and electromagnetic properties for Co_2FeO_4 spinel oxide in microwave and millimetre wave range. For this aim crystal structure was studied by X-ray measurements using X-Pert PANalytical diffractometer. Electromagnetic properties were carried out using investigation of reflection coefficient of electromagnetic in frequency range 18-110 GHz and separate study of ac dielectric and magnetic properties by investigation of complex magnetic permeability and dielectric permittivity in 4-7 GHz. frequency range.

III. RESULTS AND DISCUSSION

A. Microwave and millimetre properties.

In microwave frequency range separate measurements of dielectric permittivity $\varepsilon=\varepsilon^{/}+i\varepsilon^{//}$ and magnetic permeability $\mu=\mu^{/}+i\mu^{//}$ [$\varepsilon^{/}(\varepsilon^{//})$ and $\mu^{/}$ $(\mu^{//})$ are real (imaginary) components of dielectric permittivity and magnetic permeability, respectively] were carried our using a resonator method (diagram not shown). The samples were inserted into the measurement cell – cavity resonator. By measuring resonance frequencies f_0 and f_1 and the quality factors Q_0 and Q_1 with and without a thin sample. The thin sample was placed in maximum of ac electric field of electromagnetic wave in resonator. The $\varepsilon^{/}$ and $\varepsilon^{//}$ were determined using formulas: $\varepsilon^{/} = 1+\frac{f_1-f_0}{f_0}*\frac{V}{2\Delta V}$; $\varepsilon^{//} =(\frac{1}{Q_1}-\frac{1}{Q_0})*\frac{V}{4\Delta V}$. Here, V is the volume of the cavity resonator and ΔV is the volume occupied by the sample. The same experimental method and working formula were used for measurements of ac magnetic properties, i.e., $\mu^{/}$ and $\mu^{//}$. In this case thin sample was placed in maximum of ac magnetic field of electromagnetic wave in resonator. Fig.1. shows some distinct changes of both real and image parts of complex dielectric permittivity (Fig. 1a) and complex magnetic permeability for frequencies 4.6 GHz and 7.2 GHz as a function of annealing temperature of the samples. According to earlier report [9] coexistence of Fe rich spinel phase and Co rich spinel phase takes place by annealing temperature below 900^{0}C. Single phase state takes place for annealing temperature between 900 -950^{0}C. For annealing temperature over 950^{0}C again there is a coexistence of both phases. Coexistence of Fe rich spinel phase and Co rich spinel phase is also reflected with changes of lattice parameters and (311) peak height ratio. Such structural changes can lead to changes in dipole polarization not only within same spinel phase, but also between two coexisting phases. The generation of polarization as an effect of structural changes results in a systematic increase of $\varepsilon^{/}$ with maximum at annealing temperature about 950^{0}C and absorption part $(\varepsilon^{//})$ shows a minor change in the single phase state (900-950^{0}C). It is interesting to note that both real and image parts of complex magnetic permeability have shown large changes for the samples with annealing temperature about 860^{0}C, where as large change of complex

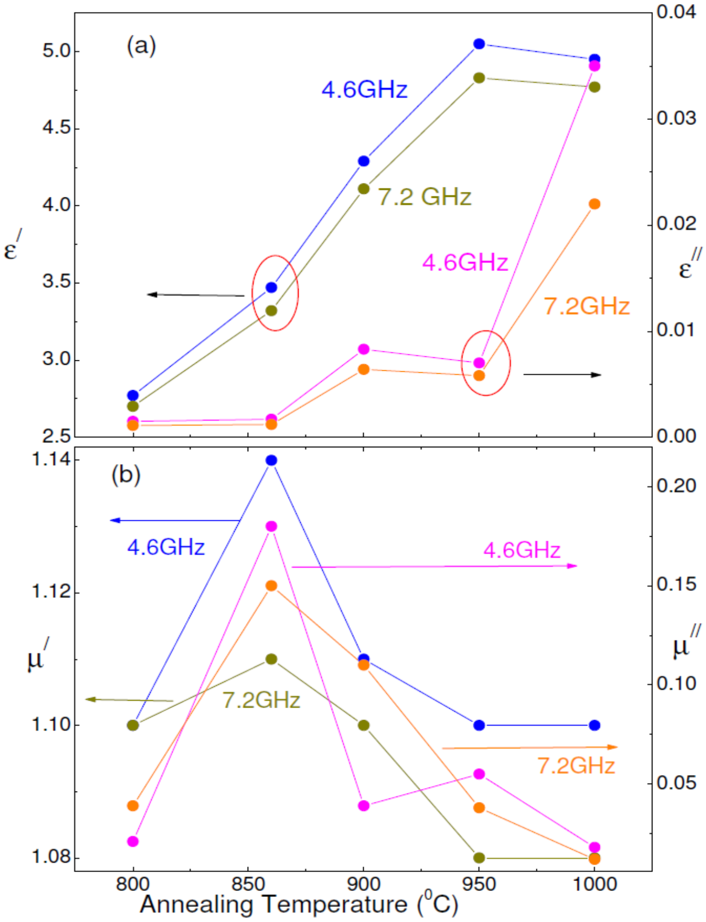

Fig. 1. (Colour online) shows the dependence of complex dielectric permittivity (a) and magnetic permeability (b) for frequencies 4.6 GHz and 7.2 GHz as a function of annealing temperature.

dielectric permittivity occurred at about 950^{0}C (single phase compound). It is possible to suppose that changes of complex magnetic permeability are connected with dependence of obtained magnetic structure on annealing temperature.

B. Measurements of complex reflection coefficient in frequency range 18 – 37 GHz.

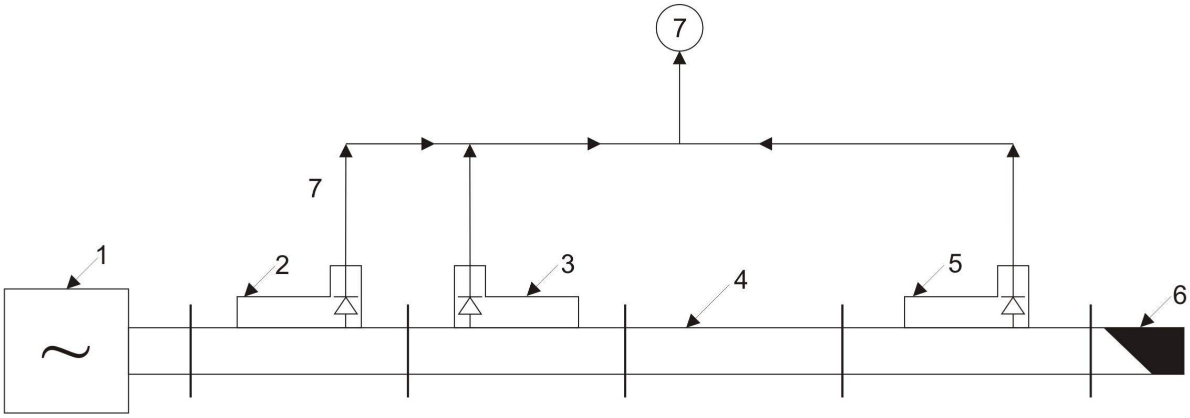

Fig. 2. 1- panoramic VSWR and attenuation meter, 2 – directional coupler of the incident wave, 3 – directional coupler of the reflected wave, 4 – waveguide section with the sample, 5 – directional of the transmitted wave, 6 – matched load, 7 – detector cells (circuits, heads) with indicator unit.

The set up, as described in Fig. 2, was used to investigate the complex refraction coefficient N= n+ im, where n and m are real and imaginary parts, respectively. Reflected *R* and transmitted *T* coefficients (by power) were measured for waveguide section 4 with cross section 7.2x3.4 mm^2 with the samples. For measurement of R we adjust the length of waveguide section *l* to meet condition for absence of interference, i.e., $\alpha l > 10$ dB and m << n. In case *R* and *T* can be found from: $T= (1-R)2e^{-2\alpha l}$, $R = \gamma_0-\gamma\gamma_0+\gamma^2$, $\gamma_0^2= k^2-g^2$, $\gamma^2= k^2*(N^2-g^2)$, where: k= 2πfc, c is velosity of light, g is transverse wave number. For H_{10} wave in rectangular waveguide g =π/a, a is size of the wide side.

As shown in Table, the electromagnetic response of Co_2FeO_4 spinel oxide at higher frequency range is very unusual. The refractive index (n) is found to be large for S95 samples, which is well stabilized in single phase. In frequency range 26-37 GHz, a monotonous drop of electromagnetic absorption (L) with increase of frequency was found. Such dependence can be resulted from magnetic resonance in frequency range from 7 to 18 GHz or some other magnetic excitation. No distinct dependence on external magnetic field up to 1 kOe was found.

Samples	n (26-37 GHz)	L (dB/mm) at 26 GHz	L (dB/mm) at 37 GHz
S100 (l =1.37 mm)	3.0±0.2	4.7 ±0.5	2.0±0.3
S95 (l = 0.65 mm)	4.5±0.3	3.0±0.7	1.9±0.3
S90 (l =1.35 mm)	2.4±0.1	4.3±0.5	1.2±0.3
S80 (l =1.02 mm)	2.5±0.2	4.0±0.7	1.7±0.3

IV. CONCLUSIONS

Structural, ac dielectric, ac magnetic and electromagnetic properties of Co_2FeO_4 spinel oxide were studied. Unusual dependence of electromagnetic properties in frequency range 26-37 GHz and distinct dependence of ac dielectric, and ac magnetic properties on annealing temperature were found. There is a lack of experimental data in literature for this material and detail interpretation needs more experimental data, which are on progress.

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