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The effect of non-magnetic Al^{3+} ions on the structure and electromagnetic properties of MgCuZn ferrite

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ABSTRACT

A series of Al substituted MgCuZn ferrite powders with composition $Mg_{0.3}Cu_{0.2}Zn_{0.52}Al_xFe_{1.98-x}O_{3.99}$ ($0.00 \le x \le 0.06$) have been synthesized with nano-sized precursor powders through the nitrate–citrate auto-combustion route. These powders were calcined, compacted and sintered at 900 °C for 4 h. X-ray diffraction patterns show the formation of cubic spinel structure. Infrared spectra indicate two fundamental absorption bands corresponding to the tetrahedral and octahedral complexes, respectively. A significant increase in density and grain size is observed with increasing Al content. The room temperature saturation magnetization increases for $x=0.015$ and then decreases for further increase in Al substitution. The initial permeability increases with the Al content attributed to the increase in the grain size and density. Curie temperature is found to be dependent on the Al concentration and it decreases due to decrease in the number of super-exchange interactions between Fe^{3+} ions in the tetrahedral and octahedral sites.

1. Introduction

Recently, multilayer chip indicators (MLCIs) have been developed for miniaturization of electronic circuits in cell phones, video cameras, notebooks, computers, etc. They are fabricated by coating and then co-firing alternate layers of ferrite and silver electrode below silver melting point (961 °C) to prevent the interfacial diffusion of silver [1].

Ni–Cu–Zn ferrite is considered as one of the most versatile magnetic materials for MLCIs applications because of their good performance in the high frequency range [2,3]. MgCuZn ferrite is potential candidate material for fabrication MLCIs at low firing temperature (below silver melting point) due to their high electrical resistivity, relatively low sintering temperature and high Curie temperature [4–6].

MgCuZn ferrite powder is usually synthesized by solid-state reaction method with sintering temperature above 1050 °C [7] which is high for MLCI applications. A typical feature of low-firing ferrite compositions is the use of sinter-active nanoscale ferrite powders prepared by chemical routes; because nanoscale powders have potential to tailor shrinkage versus temperature behavior. Bhosale and Choudhari [8] decreased the sintering temperature of MgCuZn ferrite to 1000 °C by using the nano-sized powder. Another approach to obtain low-firing and dense ferrite samples is the compositions with a small iron deficiency. It was shown that Fe-deficient substoichiometric compositions exhibit enhanced densification [9,10]. Topfer and et al. [10–13] have reported a systematic study on MeCuZn ferrites (Me=Ni and Mg) with small iron deficiency of composition $Me_{0.2}Cu_{0.2}Zn_{0.6+z}Fe_{2-z}O_{4-(z/2)}$ ($0 < z < 0.06$). They reported that the small iron deficiency significantly enhances the density of sintered samples and decreases the temperature of maximum shrinkage rate from $T=1000$ °C for $x=0$ towards lower temperatures down to $T=900$ °C for a Fe-deficient ferrite with $z=0.02$. They also reported that the initial permeability increases up to $z=0.02$ and decreases with increase in iron deficiency (z) and the optimum value for z is equal to 0.02.

The magnetic properties of soft ferrites such as NiZn ferrite and MgZn ferrite, are strongly dependent on their composition. The effect of substituting trivalent ions like Al^{3+} for Fe^{3+} in soft ferrites have been studied by many authors [14–16]. They reported that the large amount of Al substitution for Fe leads to undesirable decrease in magnetization and permeability; but some other authors [17,18] have been reported that a very small doping of Al can modify the structural and magnetic properties of soft spinel ferrites.

According to the above discussions, the aim of this work is to study the effect of Al ions substitution on the structural and

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magnetic properties of $Mg_{0.3}Cu_{0.2}Zn_{0.52}Al_xFe_{1.98-x}O_{3.99}$ ferrite prepared by sol–gel auto-combustion method.

2. Experimental method

Nanoparticles of $Mg_{0.3}Cu_{0.2}Zn_{0.52}Al_xFe_{1.98-x}O_{3.99}(0.00 \le x \le 0.06)$ ferrite were prepared through nitrate–citrate auto combustion technique using the analytical grade $Mg(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and citric acid. First, the metal nitrates were dissolved in deionized water by stoichiometric ratio. Then, an aqueous citric acid solution was added to the mixture in 1:1 M ratio of nitrates to citric acid. After adjusting the pH value with ammonia to 7, the resultant solution was heated at 80 °C under constant stirring to transform into a xerogel. During the heating process, the dried gel burnt out in a self-propagating combustion manner to form a fluffy powder. The as-burnt precursor powder was calcined at 600 °C in air for 2 h, granulated using 2 wt% PVA as a binder and uniaxially pressed at a pressure of 2 ton/cm^2 to form toroid (14 and 7 mm outer and inner diameter, respectively). Finally the pressed samples were sintered at 900 °C for 4 h.

The phase formation of samples was identified using X-ray diffraction (XRD; Cu-$K\alpha$ radiation, $\lambda = 1.5418$ Å). The X-ray density was calculated according to the formula $\rho_x = 8\,M/N_A a^3$, where M is the molecular weight of composition, N_A is the Avogadro's number and 'a' is the lattice parameter. The bulk density of sintered samples was determined by the Archimedes method. The microstructure was investigated by use a scanning electron microscope (SEM). The static magnetic properties of the samples were measured in room temperature using a vibrating sample magnetometer (VSM). The complex permeability and relative quality factor (Q) of toroids were carried out by a RF-Impedance analyzer (HP-4991A) with test fixture (Agilent 16453A) in a frequency range 1–80 MHz.

3. Results and discussion

3.1. Phase analysis

Fig. 1 shows the X-ray diffraction patterns of the sintered samples. The XRD patterns reveal the well-defined sharp Bragg peaks. All diffraction peaks can be indexed using the standard JCPDS card No. 08-0234, that confirms the formation of cubic spinel structure. This result is in agreement with earlier studies by Mürbe and Töpfer [11]. They discovered that, in $Me_{0.2}Cu_{0.2}Zn_{0.6+z}Fe_{2-z}O_{4-(z/2)}$ system ($z = 0.00, 0.02, 0.04, 0.06$), the XRD pattern of the sample with $z = 0.02$ shows single-phase ferrite.

The lattice parameter values of the samples are listed in Table 1. It is seen that the lattice parameter 'a' gradually decreases with increasing Al content. Similar behavior was observed on Al-substituted Ni–Zn [14], Zn [19] and NiCuZn ferrites [17]. The decrease of the lattice parameter is attributed to the ionic radii of Fe^{+3} and Al^{+3}. According to Shannon [20] the ionic radii for Al^{3+} and Fe^{3+} are 0.535 and 0.645 Å.

3.2. FT-IR analysis

FT-IR spectroscopy is an important technique to identify the stretching and bending vibrations of tetrahedral and octahedral complexes of spinel structures. IR spectra of the samples presented in Fig. 2 show two absorption bands in the range of about 400–600 cm^{-1}. The higher wave number absorption band ν_1 attributed to the vibrations of iron ions in the tetrahedral position, is in the range of 567–570 cm^{-1}. The lower wave number absorption band ν_2 associated with the iron ions in the octahedral site, is in the range of 412–426 cm^{-1}. These bands are the common features of all the ferrites [21]. The positions of ν_1 and ν_2 bonds are listed in Table 1. It is obvious from table that, as the Al content increases, ν_1 remains almost constant while ν_2 increases. Similar type of variation in band positions for Al substituted NiCuZn ferrite is reported by Eltabey et al. [17]. These results reveal that the radius of octahedral site, r_B, decreases with Al content where the band frequency is inversely proportional to the bond length [22].

Table 1
Lattice parameter (a), X-ray density (ρ_x), bulk density (ρ_b), grain size (D), FT-IR spectral data ν_1 and ν_1, number of magnetic moment (n_B) and Yaffet–Kittel angle of the sintered samples.

Al cont. (x)	0.00	0.015	0.030	0.045	0.060
a (°A)	8.56	8.51	8.48	8.43	8.39
ρ_x (g/cm^3)	4.83	4.91	4.96	5.03	5.10
ρ_b (g/cm^3)	4.45	4.48	4.52	4.64	4.69
D (μm)	0.71	0.91	1.38	2.04	2.22
ν_1 (cm^{-1})	568	568	570	569	567
ν_2 (cm^{-1})	412	418	422	420	426
n_B (μ_B)	2.02	2.22	2.15	2.03	1.97
α_{Y-K} (deg)	55.5	53.3	53.5	54.2	54.4

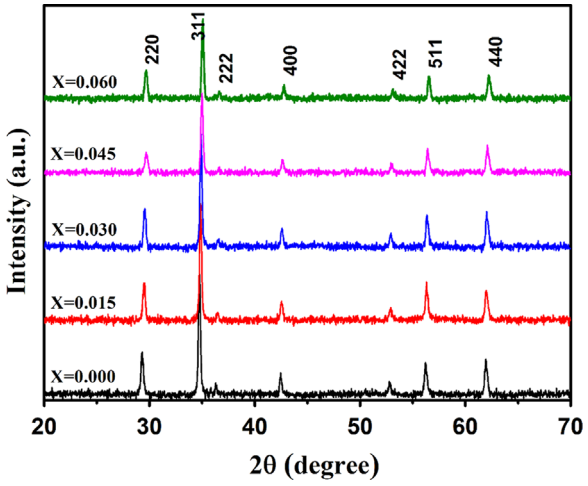

Fig. 1. X-ray diffraction patterns for $Mg_{0.3}Cu_{0.2}Zn_{0.52}Al_xFe_{1.98-x}O_{3.99}$ ferrites.

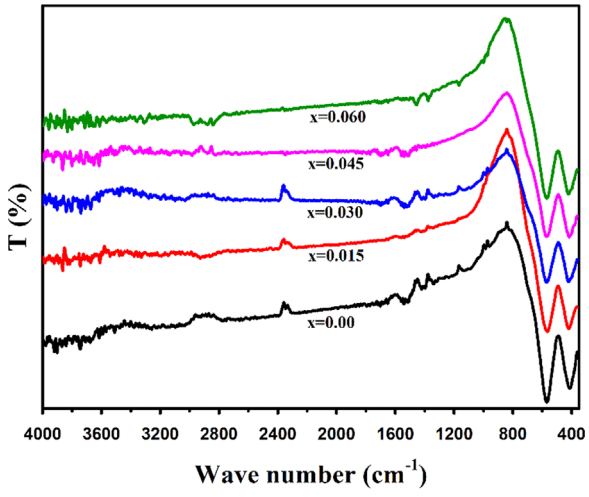

Fig. 2. FT-IR spectra for $Mg_{0.3}Cu_{0.2}Zn_{0.52}Al_xFe_{1.98-x}O_{3.99}$ ferrites in the range of 4000–350 cm^{-1}.