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Structural, electrical and magnetic study of nanocrystalline Ti-substituted Zn–Mn ferrospinels

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ABSTRACT

Titanium substituted Zn–Mn ferrites were prepared by sol–gel route. Formation of single phase cubic spinel structure for all the compositions was confirmed from their X-ray diffraction studies. These ferrite samples existed as uniform and homogenous grain size as observed from scanning electron microscopy technique (SEM). The magnetic studies indicated that, the ferrimagnetic behavior increases with titanium substitution. Dielectric constant and complex impedance were measured as a function of frequency in the range 20 Hz–1 MHz. Frequency dependence of dielectric constant shows dielectric dispersion due to the Maxwell–Wagner type of interfacial polarization and impedance study reveals that the electrical conduction in the ferrites is by the interior of the grain boundaries. In general, the substitution of titanium plays an important role in changing the structural, magnetic and electrical properties of these ferrites.

1. Introduction

Semiconducting ferrites are well-studied materials and its wide range of commercial applications, due to their interesting structural, electrical and magnetic properties. They are extensively used in microwave devices, information storage systems, magnetic cores and several medical diagnostic purposes because of high electric resistivity, low eddy current and low dielectric losses [1–3]. In ferrites the distribution of the different ions in the tetrahedral and octahedral sites of the spinel lattice mainly depends on the method of preparation and processing conditions. The dielectric properties of these ferrites are mainly dependant on the method of preparation and substitution of various cations in them. Ferrite prepared by a ceramic route involves high-temperature and the particles obtained rather large and non-uniform in size. In order to overcome these difficulties, wet chemical methods like sol–gel method has several advantages over others for preparation of nanosized metal oxides as the process begins with a relatively homogeneous mixture and involves low temperature conditions resulting in a uniform ultrafine porous powder [4–6]. The advantages of nanosized ferrites are that it is possible to sinter them at relatively low temperatures for a short duration, which saves time, cost, and other factors such as volatility occurring at higher sintering temperatures. Nanosized ferrites are expected to give higher sintered density at relatively lower sintering temperatures, without considerable grain growth. A number of investigators have studied the frequency dependent dielectric permittivity, dielectric loss tangent, and ac conductivity of Li–Mn [7], Zn–Mn–Fe [8] and Li–Cr [9] ferrite system. However, literature survey indicates that, effect of Ti substitution on dielectric properties and complex impedance of Zn–Mn ferrite has not yet been studied. Hence, we have investigated the nanosized $ZnMn_{1-x}Ti_xFeO_4$ ($1.0 \geq x \geq 0$) system synthesized by the sol–gel method with a view to understand the effect of Ti substitution on its structural, magnetic and dielectric properties. The variation in saturation magnetization with Ti content is also reported.

2. Experimental technique

Polycrystalline sample having the general formula, $ZnMn_{1-x}Ti_xFeO_4$ (where $x=0.0$, 0.25, 0.50, 0.75 and 1.0) were synthesized by sol–gel method. The titanium oxynitrate, iron nitrate, zinc nitrate, manganese nitrate and citric acid were mixed in the required stoichiometric ratios in distilled water. The pH of the solution was maintained between 9 and 9.5 using ammonia solution. The solution mixture was slowly heated around 373 K with constant stirring to obtain a fluffy mass. This precursor powder was sintered at 973 K for 8 h. The sintered powders were

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granulated using 2% polyvinyl alcohol as a binder and were uniaxially pressed at a pressure of 8 t/cm^2 to form pellets. These pellets were gradually heated to about 773 K to remove out the binder material.

The phase formation of the samples was confirmed by X-ray diffraction studies using Philips PW-1710 X-ray diffractometer with CUKα radiation (λ=1.54047 Å). The surface morphology of the ferrite sample was studied by using (JEOL-JSM 6360) scanning electron microscope (SEM). The magnetic property of the sample was studied by vibrating sample magnetometer (VSM). The frequency dependent dielectric permittivity and complex impedance was measured in the frequency range of 20 Hz–1 MHz by HP 4284-A LCR precision meter bridge in parallel mode. Silver paste was applied on both sides of the pellets for good ohmic contacts.

3. Results and discussion

3.1. XRD studies

Fig. 1. depicts the powder XRD patterns of the prepared $ZnMn_{1-x}Ti_xFeO_4$ compositions. All the observed reflections of the Ti substituted Zn–Mn ferrite samples could be assigned to cubic spinel phase. The lattice parameters were calculated for the cubic phase using following relations.

a) For cubic phase $a=d(h^2+k^2+l^2)^{1/2}$

Where, a=Lattice parameters, (hkl)=Miller indices

d=interplanar distance

It is observed that the unit cell parameter of the Ti substituted Zn–Mn ferrite gradually increases with increasing Ti content in the composition. The slow linear increasing trend in the lattice parameter is attributed to the replacement of Mn^{3+} (0.65 Å) ion by Ti^{3+}, a slightly larger ion (0.67 Å), in the system of

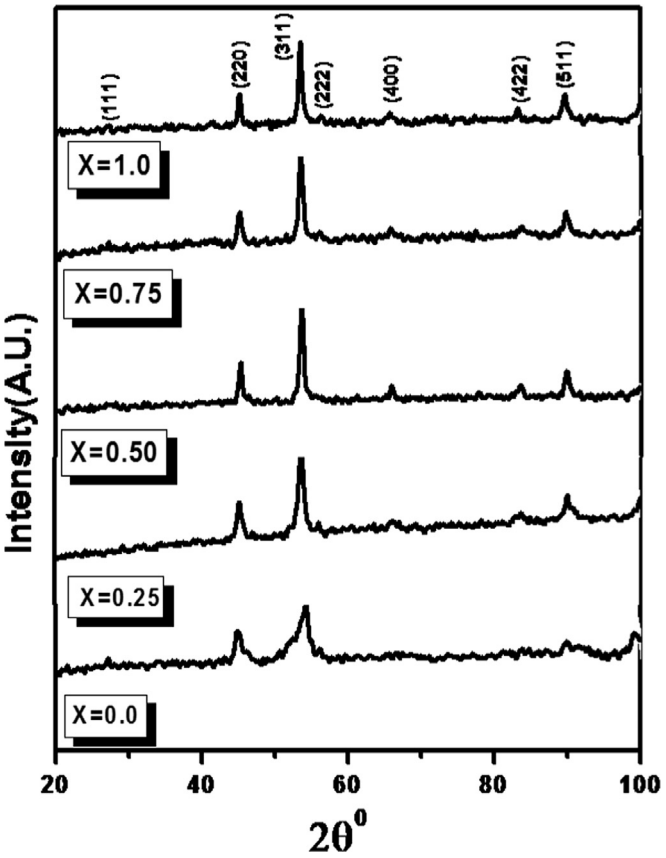
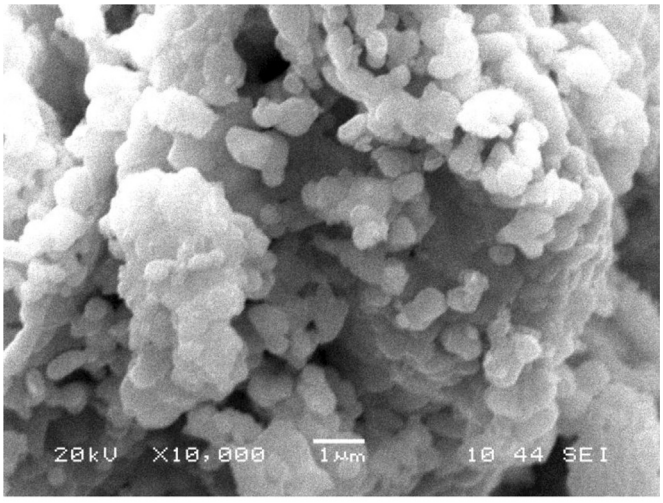


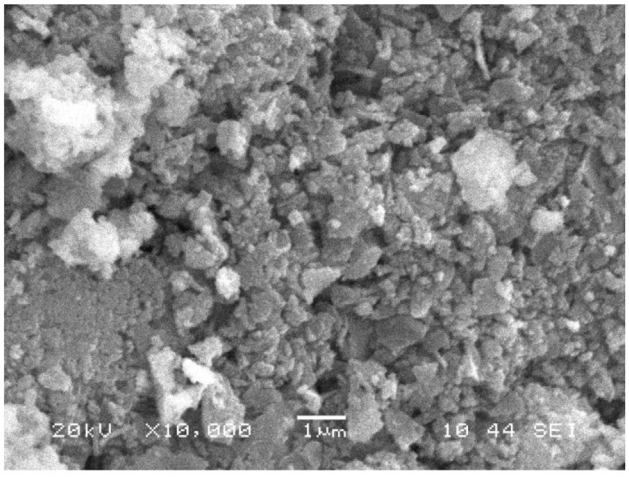
Fig. 1. X-ray diffraction pattern of $ZnMn_{1-x}Ti_xFeO_4$.

Table 1
Lattice constant, crystallite size and X-ray density for $ZnMn_{1-x}Ti_xFeO_4$ system.

Composition (x)	Lattice constant (a) nm	Crystallite size (t) nm	X-ray density (dx) gm/cm^3
0.0	8.413	30	4.85
0.25	8.415	31	4.87
0.50	8.422	32	4.93
0.75	8.427	34	4.98
1.0	8.431	38	5.01



a) x = 0.0



b) x = 1.0

Fig. 2. SEM micrographs of the system $ZnMn_{1-x}Ti_xFeO_4$.

$ZnMn_{1-x}Ti_xFeO_4$ [10]. The slow increasing trend of unit cell parameter and a gradual increase in the X-ray density with increase in titanium content is observed. From the X-ray diffraction peaks, average particle size was estimated using Scherrer's formula.

$$t = 0.9\lambda/\beta \text{ Cos } \theta$$

where 0.9 is the Scherrer's constant (k), λ is the X-ray wavelength corresponding to CrKα, β denotes the full-width at half-maximum of the peak and θ is the Bragg angle. The crystallite size was found to be in the range of 25–30 nm. The X-ray density (dx) was calculated using the relation,

$$dx = 8\ M/Na^3$$