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Magnetic and dielectric properties of nanophase manganese-substituted lithium ferrite

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ABSTRACT

Nanocrystalline manganese-substituted lithium ferrites viz. $Li_{0.5}Fe_{2.5-x}Mn_xO_4$ ($2.5 \leq x \geq 0$) were prepared by sol–gel autocombustion method. X-ray diffraction analysis confirmed that as the concentration of manganese increases the cubic phase changes to the tetragonal phase. The variation of saturation magnetization was studied as a function of manganese content. All the compositions indicate that they are ferrimagnetic in nature. The dielectric constant, dielectric loss tangent and ac conductivity of all samples were measured at room temperature as a function of frequency. These parameters decrease with increase in frequency for all of the samples. The substitution of manganese plays an important role in changing the structural and magnetic properties of these ferrites. The compositional variation of dielectric constant and d.c. resistivity shows an inverse trend of variation with each other.

1. Introduction

The polycrystalline ferrites have very important structural, magnetic and electrical properties that are dependent on several factors such as method of preparation, substitution of cations and microstructure, etc. Lithium ferrite and substituted lithium ferrites have interesting technological applications such as, cathode materials in lithium ion batteries [1–3]. They are used in microwave applications due to their high resistivity and low eddy current losses [4,5].

Many workers have studied the frequency dependence of the dielectric constant, dielectric loss tangent and ac conductivity of Li–Ni [6], Li–Co [7], Li–Mg [8] and Li–Ge [9] ferrite systems. However, no reports have been found in the literature on dielectric properties of Mn-substituted lithium ferrites. In the present work, the influence of manganese substitution on structural, magnetic properties, dc resistivity and dielectric properties of $Li_{0.5}Fe_{2.5-x}Mn_xO_4$ ferrite samples (where $x = 0.0$, 0.5, 1.0, 1.5, 2.0 and 2.5) is reported.

2. Experimental

2.1. Sample preparation

Polycrystalline ferrite samples having the general formula, $Li_{0.5}Fe_{2.5-x}Mn_xO_4$ ($x = 0.0$, 0.5, 1.0, 1.5, 2.0 and 2.5) were synthesized by sol–gel autocombustion method. High-purity AR grade ferric nitrate, manganese nitrate, lithium nitrate and citric acid were used for synthesis. The metal nitrate solutions were mixed in the required stoichiometric ratios in distilled water. The pH of the solution was maintained between 9 and 9.5 by using ammonia solution. The solution mixture was slowly heated to 100 °C with constant stirring to obtain a fluppy mass. The precursor powder was sintered at 700 °C for 8 h. The sintered powder was mixed with 2% polyvinyl alcohol as a binder and uniaxially pressed at a pressure of 8 t/cm^2 to form pellets.

2.2. Characterizations

The phase formation of the samples was confirmed by X-ray diffraction studies using a Philips PW-1710 X-ray diffractometer with CuKα radiation ($\lambda = 1.54056$ Å). The high field hysteresis loop tracer was used to measure the saturation magnetization of the samples. The dc resistivities of the samples were measured at room temperature by two probe method. The dielectric constant,

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dielectric loss tangent and ac conductivity were measured in the frequency range 20 Hz–1 MHz at room temperature using a HP4284 A LCR Meter. Silver paste was applied to both the surfaces of the pellets for good ohmic contacts.

The lattice parameters were calculated for the cubic and tetragonal phase using following relations:

$$\text{(a) for cubic phase } 1/d^2 = h^2 + k^2 + l^2/a^2 \quad (1)$$

$$\text{(b) for tetragonal phase } 1/d^2 = h^2 + k^2/a^2 + l^2/c^2 \quad (2)$$

where a and c is the lattice parameter; $(h\,k\,l)$ the Miller indices and d the interplanar distance.

The particle size was estimated using Scherrer's formula:

$$t = 0.9\lambda/\beta\cos\theta \quad (3)$$

where symbols have their usual meaning.

The X-ray density was calculated according to the formula

$$dx = 8\,M/Na^3 \quad (4)$$

where 'M' is the molecular mass, 'N' the Avogadro's number and 'a' the lattice parameter which was calculated from the X-ray diffraction pattern.

The percentage porosity of sample was calculate using the formula

$$P(\%) = (d_x - d_a/d_x) \times 100 \quad (5)$$

where d_x is the X-ray density and d_a the actual density.

The surface area was determined by using following relation:

$$s = 6/\rho d \quad (6)$$

where 'ρ' is the X-ray density, 'd' average particle size and 's' the surface area.

The capacitance and loss tangent were measured at room temperature in the frequency range from 20 Hz to 1 MHz, to calculate the dielectric constant (ε') and the AC conductivity (σ_{ac}) by the following formulae:

$$\varepsilon' = Cd/\varepsilon_0 A \quad (7)$$

$$\sigma_{ac} = \varepsilon'\varepsilon_0\omega\tan\delta \quad (8)$$

where 'C' is the capacitance of the sample, 'd' the thickness of the sample, 'A' the cross-sectional area, 'ε_0' the permittivity of free space and $\omega = 2\pi f$, i.e. angular frequency.

3. Results and discussion

3.1. X-ray diffraction study

X-ray diffraction patterns of manganese-substituted lithium ferrite powders are shown in Fig. 1. The diffraction patterns and data indicate that, upto Mn = 1.5 the samples are cubic crystal structure while, above $x = 1.5$ they are tetragonal in nature. The tetragonal phase for $x = 2.0$ and 2.5 is attributed to Jahn–Teller effect by Mn^{3+} ions with d^4 electron configuration [10–12] and also to the fact that more than 50% manganese ions at the 'B' sites cause tetragonal distortion in the lattice. The variation of the lattice parameter can be explained on the basis of an ionic size difference of the component ions. Initially the lattice parameter 'a' increases with Mn content. The larger Mn^{3+} ions (0.645 Å) successively replace the smaller Fe^{3+} ions (0.64 Å) on B sites due to the site preference [13]. This results in an expansion of unit cell to accommodate larger ions and hence the lattice constant increases. X-ray density initially decreases and then after increasing the manganese substitution it increases. The X-ray density is in the range 5.08–4.72 g/cm^3. The data on lattice constant (a), X-ray density (dx), crystallite size (t), porosity (P) and surface area (s) for the samples manganese-substituted lithium ferrites are given in Table 1.

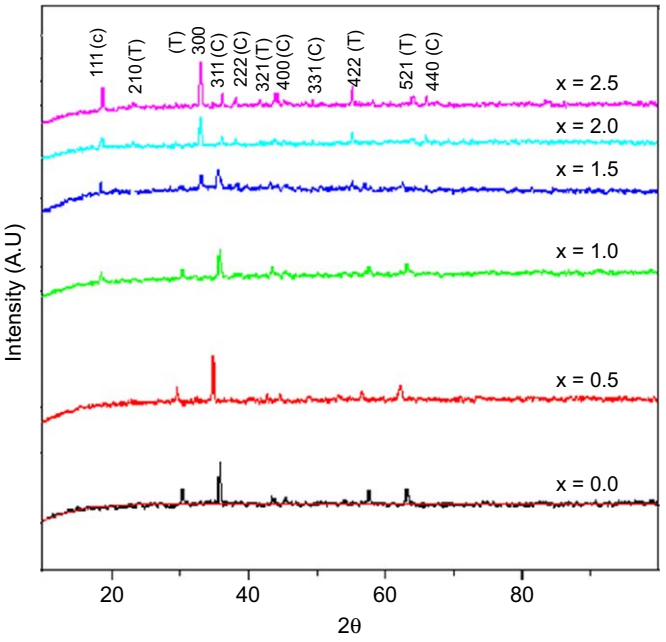

Fig. 1. X-ray diffraction patterns of $Li_{0.5}Fe_{2.5-x}Mn_xO_4$.

3.2. Variation of saturation magnetization (Ms) with Mn content

Fig. 2 shows the variation of saturation magnetization with Mn content. The saturation magnetization decreases with increasing concentration of manganese ions due to the fact that the A–O–A interaction becomes weak and A–O–B interaction becomes strong in Mn-substituted lithium ferrites [14]. The presence of Yafel-Kittel arrangement of magnetic moments on the octahedral sites and the stronger covalency effect arising due to various cationic site dimensions are also responsible for the same. Similar type of variation was observed by Yen-Pei Fu et al. in Li–Mn ferrites [14] and Li–Al ferrites [15].

3.3. Dielectric properties

3.3.1. Dielectric constant (ε') at room temperature with frequency

The variation of dielectric constant as a function of frequency is shown in Fig. 3. The dielectric constant decreases continuously with increase in frequency for all the samples. The variation of dielectric constant with frequency indicates the dispersion due to the Maxwell–Wagner type [16,17] of interfacial polarization in accordance with Koop's phenomological theory [18]. A close examination of the figures indicates that the dispersion of 'ε' with frequency is maximum in the case of lithium ferrite and the dispersion decreases due to substitution of manganese content. A similar variation of the dielectric constant with frequency was observed by Reddy [19] in the case of Li–Ni ferrites, by Murthy and Sobhanadry [20] in the case of Ni–Zn ferrites, by Venudhar [7] in the case of Li–Co ferrites and Shaikh et al. [21] in the case of Li–Mg–Zn ferrites. Iwauachi [22] and Rabkin and Novikova [23] have pointed out that there is a strong correlation between the conduction mechanism (hopping) and the dielectric behavior of ferrites. By electronic exchange, $Fe^{3+} \leftrightarrow Fe^{2+}$ and $Mn^{2+} \leftrightarrow Mn^{3+}$, one obtains local displacement of the electrons in the direction of applied electrical field. These displacements determine the polarization of the ferrites.