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# Tuning magnetic and high frequency dielectric behavior in Li-Zn ferrites by Ho doping

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## ABSTRACT

In the present study, the impact of holmium (Ho) substitution on structural, spectral, dielectric and magnetic behavior of  $\text{Li}_{1-2x}\text{Zn}_{0.4}\text{Ho}_x\text{Fe}_{2-x}\text{O}_4$  ( $0.00 \leq x \leq 0.15$ ) ferrites was investigated. The development of spinel phase and structural changes induced by Ho doping were confirmed by X-ray diffraction. The accommodation of Ho ions into spinel lattice was restricted for  $x \geq 0.06$  as indicated by ortho phase ( $\text{HoFeO}_3$ ) traces. The decrease in lattice parameter ( $a$ ) was attributed to the segregation of Ho ions on grain boundaries. FTIR spectra featured two intrinsic vibrational bands  $\nu_1$  ( $617 \text{ cm}^{-1}$ ) and  $\nu_2$  ( $488 \text{ cm}^{-1}$ ) for  $x = 0$  due to tetrahedral and octahedral vibrations respectively. The compositional dependence of force constants and bond lengths has explained on the basis of cations distribution and oxygen-cation bond distances of respective sites. The addition of Ho ions decreased the saturation magnetization and optimized the coercivity from 59 to 335 Oe, proposing these ferrites for magnetic recording media. Dielectric results for the entire range of frequency (1 MHz to 3 GHz) revealed that ac conductivity increased from  $3.5 \times 10^5$  to  $1.8 \times 10^6$  ( $\Omega\text{-cm}$ )<sup>-1</sup> up to  $x = 0.09$  and then it decreased slightly for  $x = 0.12$ . The effective contribution of grain-interior mechanism to dielectric behavior was confirmed by complex impedance study. The results of dielectric studies displayed that Ho doped lithium ferrites are suitable low loss potential materials for high frequency based applications.

## 1. Introduction

Soft ferrites with the spinel structure are fascinating the modern industry of electronic materials by offering unusual properties in the nano scale regime. The spinel ferrites are more valuable than other materials in the field of nanotechnology due to their low dielectric and magnetic losses, high electrical resistivity and high values of saturation magnetization. The properties of spinel ferrites are greatly affected by the way they synthesized, cations distribution amongst the tetrahedral and octahedral sites, sintering temperature, chemical composition etc [1,2]. Lithium ferrite with an inverse spinel structure has become as one of the most important microwave devices based application unit. Lithium ferrites have extensive applications in passive microwave components, such as circulators, isolators, phase shifters and miniature antennas over wide frequency range [3,4].

Relatively high electrical resistivity, high Curie temperature, high saturation magnetization, lower densification temperature and low

dielectric and magnetic losses of these ferrites offer great advantages over other spinel ferrites [3,5–7]. However, the use of these soft ferrites primarily in microwave devices is restricted due to the difficulties encountered during the synthesis and sintering processes. Lithium and oxygen become volatile at high sintering temperature ( $> 1273 \text{ K}$ ) which results into high dielectric loss and low magnetic properties [8,9]. The irreversible loss of oxygen and lithium during sintering creates difficulties to achieve high densities in stoichiometric form. So, the adoption of a suitable synthetic route plays a key role to produce ultrafine powders with uniform size, chemically homogeneous composition and high production rate. The auto citric sol-gel synthetic method offers an easy alternative for the synthesis of nanocrystalline lithium ferrites at low sintering temperature in a relatively shorter time [10–14].

Moreover, it has been predicted that properties like electrical and thermal conductivity, structural, spectral, dielectric and magnetic response of these materials could be improved by substituting them with

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rare-earth (RE) elements. The conduction mechanism in spinel ferrites is governed by the 3d electrons spin coupling which arises from Fe-Fe interactions. However, when  $\text{Fe}^{3+}$  ions on octahedral sites of spinel lattice are partially substituted by rare earth ions, the Fe-RE interactions resulted into 3d-4f coupling. This strong coupling between 3d-4f electrons can tailored the electromagnetic properties of these materials due to orbital shape of 4f-unpaired electrons [15]. Substitution of divalent and trivalent cations into spinel lattice of lithium ferrites reduces dielectric losses ( $\leq 10^{-2}$ ) which cannot be attained in pure Li-ferrites due to poor densification behavior [16]. In substituted lithium ferrites, the incorporation of  $\text{RE}^{3+}$  ions for Fe ions reduces the probability of  $\text{Fe}^{2+}$  formation, and leads to a high electrical resistance, high thermal stability and low values of dielectric losses [17]. The motive to substitute holmium is its large intrinsic magnetic moment ( $10.6 \mu_B$ ) and strong anisotropy field. For such a case, spins are forced to align along the local anisotropic axis which leads to various magnetic ordering in ferrite system. Moreover, substitution of highly resistive holmium ions can possibly increase the electrical resistivity of material and reduce the magnetic as well as dielectric losses which will support the system for use in high frequency applications such as microwave absorbing devices [18–20].

In previously reported work on lithium based ferrites, the researchers have explored the influence of various rare earth ions substitutions on the electromagnetic properties of Li-Ni, Li-Mg, Li-Zn, Li-Co ferrites etc [21–27]. The literature survey has confirmed that no investigation is available to check the influence of  $\text{Ho}^{3+}$  ions substitution into Li-Zn ferrites with view to their structural, spectral and high frequency dielectric characteristics. In the present study, a detailed investigation of Ho substituted Li-Zn ferrite has been carried out which results in the modifications of their properties.

## 2. Materials and methods

Li-Zn ferrites with compositional formula  $\text{Li}_{1.2}\text{Zn}_{0.4}\text{Ho}_x\text{Fe}_{2-x}\text{O}_4$  ( $x = 0.00\text{--}0.15$ ) were synthesized by sol-gel auto combustion method.  $\text{LiCl}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  of reagent grade purity were employed to incorporate required metal ions. Holmium nitrate penta hydrate ( $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ) was added as a supply of  $\text{Ho}^{3+}$  ions. Suitable stoichiometric quantities of all metal nitrates,  $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and citric acid were first dissolved in deionized water. Molar ratio of citric acid to nitrates was taken as 2:1. A little quantity of concentrated ammonia ( $\text{NH}_3$ ) was then added to adjust the PH of solution up to 7. All through this process, the solution was constantly stirred via a magnetic agitator. Next, the solution was heated at 353–363 K under constant stirring to convert into a xerogel. Finally, xerogel self ignited and burned in an auto combustion manner until dried gel was burned entirely out to make fluffy powder. The final powders were then calcined at 1223 K for 6 h for spinel phase formation with a face centered cubic (fcc) structure. To prepare the pellets, the synthesized powders of ferrite were mixed with 5 wt% polyvinyl alcohol (PVA) for binding and were uniaxially pressed to form the circular pellets at a pressure of 30 kN for 3 min. The binder was removed by sintering the pellets at 473 K for 1.5 h. The dried un-sintered powder was characterized for thermal studies at a heating rate of 283 K/min in air via a thermal analyzer (Mettler Toledo GC 200). The phase identification analysis of sintered powders was carried out using D8 Advance-Bruker X-ray diffractometer (XRD) with Cu-K $\alpha$  radiation ( $2\theta = 10\text{--}70^\circ$ ). Infrared spectra (IR) for all powders were measured on a Nicolet TM 5700 spectrophotometer, from 400 to 1000  $\text{cm}^{-1}$ . High frequency dielectric properties of sintered pellet specimens were deliberated using a Wayne Ker WK6500B impedance analyzer. Lake Shore model-7300 of vibrating sample magnetometer was used to study the magnetic characteristics of all the samples up to a maximum field of  $\pm 30$  kOe.

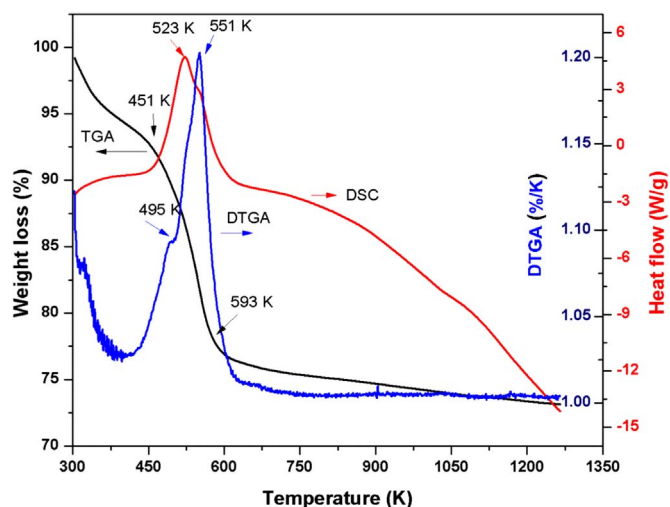


Fig. 1. Thermal analysis (TGA/DSC) of  $\text{Li}_{1.2}\text{Zn}_{0.4}\text{Ho}_x\text{Fe}_{2-x}\text{O}_4$  ferrites for  $x = 0.00$ .

## 3. Results and discussion

### 3.1. TGA analysis

Thermal decomposition of the precursors is investigated by TGA analysis (Fig. 1). Two main areas of weight loss from as prepared powder can be seen from TGA curve, First is from room temperature to about 451 K and the second is from 451 K to about 593 K. The first weight loss (8%) is attributed to evaporation of water and solvent, absorbed by the precursors during the synthesis procedure. In second area, a high weight loss (23%) is occurred which is ascribed to the removal of citric acid content and decomposition of organic components (nitrates etc). A weight reduction of about 3.5% is occurred for heat treatment from 593–1173 K. After 1173 K, no reasonable weight loss has seen which indicates the complete decomposition of nitrates and the formation of metal oxides. The entire growth of spinel phase in the un-calcined powder accomplished that no more calcinations steps are needed for the contentment of ignition process [15]. DSC curve reveals that the decomposition process is strongly exothermic in nature. The exothermic peak appeared at 523 K which is reasonably intense and sharp, indicating the maximum decomposition of metal hydroxide of the dried gel just in a single step. It has been believed that the intense exothermic peak at 523 K in the DSC curve is associated with the oxidation of hydrocarbons and an autocatalytic anionic oxidation–reduction reaction occurring between the citrate and nitrate system [28,29]. On DTA plot, two exothermic peaks coupled with weight loss are appeared at around 495 K and 551 K due to burning and disintegration of residual elements.

### 3.2. X-ray diffraction analysis

Fig. 2 displays the X-ray diffraction patterns of  $\text{Li}_{1.2}\text{Zn}_{0.4}\text{Ho}_x\text{Fe}_{2-x}\text{O}_4$  ferrites measured at room temperature. All sintered samples illustrate the characteristics Bragg reflections with most intense peak of  $hkl$  (311), confirming the formation of spinel phase fcc structure. The diffraction peaks correspond to the expected spinel structure and are indexed to the cubic lithium ferrite phase according to the standard ICDD card: 00–049–0266. It can be seen explicitly from Fig. 2 that  $\text{Ho}^{3+}$  is completely incorporated into Li-Zn ferrite up to Ho concentration  $x = 0.03$  and thereafter some secondary peaks corresponding to orthophase  $\text{HoFeO}_3$  (ICDD card: 01–074–1479) are appeared. The appearance of secondary phase might be due to the isolation of  $\text{Ho}^{3+}$  ions at the grain boundaries, signifying the solubility edge of  $\text{Ho}^{3+}$  into the spinel structure [30]. After  $x = 0.03$ , the larger radii  $\text{Ho}^{3+}$  ions do not get accommodated themselves in spinel lattice and

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