Original Article

Effect of the La$^{3+}$ ions substitution on the magnetic properties of spinal Li-Zn-ferrites at low temperature

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Abstract

The effect of La$^{3+}$ ions substitution on the magnetic properties of the composition \( \text{Li}_{0.5-x}\text{Zn}_x\text{La}_{x}\text{Fe}_{2.5-0.5x}\text{O}_4 \) \((0.02 \leq x \leq 0.1; y = 0.6)\) was studied. The structure of the samples was investigated using X-ray, SEM and IR. Both of zero field cooled (ZFC) and field cooled (FC) modes magnetization were studied at low temperature range (2 K $\leq$ T $\leq$ 400 K). Magnetization applied field-dependence (M-H) curves were measured at low temperature (5 K). The experimental data revealed that the samples exhibited a phase transition from ferrimagnetic state at low temperature to paramagnetic state at high temperature (400 K). The obtained Curie temperature was shifted to lower value with La$^{3+}$-content. The M-H curves showed that the samples are soft ferromagnetic and it can be an excellent candidate for industrial applications.

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1. Introduction

Lithium based ferrite is a promising magnetic material for many applications because of its better properties at high frequency including: high resistivity, high Curie temperature and low dielectric loss, substitution for garnets and other spinel ferrites [1-4]. These ferrites belong to a large family of spinel compounds having a general formula \( \text{AB}_2\text{O}_4 \). The properties of lithium ferrites can be tailor made by substituting them with different metal ions such as Zn, Co, Cd, Cu, Ti, etc., for microwave and hyperthermic applications [5-7]. In the preparation of lithium based ferrites, low temperature sintering is needed to suppress lithium volatility and oxygen loss during firing. The crystal structure, microstructure and cation distribution have a remarkable effect on the ferrite properties and their applied aspects [8-10]. Several studies have been reported on the effect of additions of divalent, trivalent and tetravalent ions on the magnetic and electrical conductivity of Li-ferrites [11-14].
The modification of the physical properties of ferrites due to the substitution of divalent, trivalent and tetravalent ions have been studied by several authors [15–17]. The most important factors that affect the different properties of ferrites are the radius and the magnetic moment of the substituted ion. Patil et al. [18] studied the effect of substitution of La for iron in the system CuLa2Fe2−xO4 and the detected two phases of spinel and perovskite in addition to γ-Fe2O3 and CuFeO2. In general, the rare earth ions after certain concentration, which is called the critical concentration, are too large to occupy the tetrahedral and octahedral sites [18] during the sintering process. This will form secondary phases on the grain boundaries.

In the present work, we have synthesized the Li0.5−0.5xZn0.5La0.5Fe2.5−0.5x−yO4 (0.02 ≤ x ≤ 0.1; y = 0.6) systematically with La concentration and temperature in order to explore its magnetic properties. We focused on the systematic study of the microstructure, and IR of solid solution of La-substituted lithium zinc ferrites at wide temperature range. The magnetization as a function of temperature (2K ≤ T ≤ 400K) was measured in zero field cooled and field cooled modes.

2. Experimental

High purity oxides of Fe2O3, LiOH, ZnO and La2O3 were mixed together in molar ratio to prepare ferrites of composition Li0.5−0.5xZn0.5La0.5Fe2.5−0.5x−yO4 (0.02 ≤ x ≤ 0.1) and y = 0.6 using the conventional ceramic technique. The raw materials were mixed, well grounded to fine powder using agate mortar and partially at 600°C for 5 h, then ground again and partially another time at 900°C for 9 h. The samples were pressed into pellets form using uniaxial pressure 1.9 × 10⁸ N/m² and finally sintered at 1150°C for 15 h followed by cooling to room temperature with the same rate at that of heating (100°C/h) in the Lenton furnace 16/5 UAF (UK). Some of the samples were crushed again to fine powder for magnetic measurements. X-ray powder diffraction was performed on the investigated samples using Rigaku Co-Miniflex X-ray diffractometer employing CuKα radiation with λ = 1.5418 Å. DC magnetization measurements were performed in a SQUID magnetometer (Quantum design MPMS5S). To observe the transition profiles accurately, the measurements of dc magnetization-temperature (M–T) curves were measured in ZFC (zero field cooled), FC (field cooled) modes in the temperature range between 5 and 400K with applied field (H = 1000 Oe). In addition, field-dependence magnetization was investigated at low temperature (5 K). IR spectra in the 400–4000 cm⁻¹ range was recorded at room temperature using the infrared spectrophotometer (Bruker, Vector 220).

3. Results and discussion

The X-ray diffraction patterns for the investigated samples are presented in Fig. 1. It is observed that, the single phase with cubic structure for all the concentrations. All the XRD peaks for each sample can be easily indexed by assuming cubic crystal symmetry. This result is well in agreement with the previous studies on Li-Zn-FeO3 [12,13,17]. The lattice constant, (a) has been calculated by using several peaks from XRD patterns and plotted as a function of La content (x) in Fig. 1(b). The values of (a) are agree well with JCPDS card [19], within experimental errors. Moreover, the value of (a) decreased with increases La-content. This behavior can be attributed to the ionic radii of the ingredient ions. In order to confirm the formation of the spinel phase and to understand the nature of the residual La in the samples, the FT-IR spectra of the investigated samples were shown in Fig. 2, recorded in the range 400–4000 cm⁻¹. The spectra indicated the presence of only two fundamental absorption bands ν1 and ν2 in the range from 400 to 1000 cm⁻¹, corresponding to the tetrahedral and octahedral complexes respectively, which is the common of all spinel structure [20]. This difference in the band position is expected because of the difference in the Fe⁵⁺–O²⁻ distance for the octahedral and tetrahedral compounds. It is known that [21] the vibration spectra of ferrites and it attributed the sharp absorption band around 600 cm⁻¹ to the intrinsic vibrations of the tetrahedral groups and the other band the octahedral groups. We suggest that the La doping of the Li-Zn-ferrites give the opportunity for the microwave applications because the absorption increases with the La content.

Fig. 3(a) shows the magnetization divided applied field as a function of the temperature for samples with different La-content (x = 0.02, 0.04, 0.06, 0.08, 0.1). The measurements
were done during heating after cooling with applied field (1000 Oe) from room temperature to around 2 K (Field Cold mode). The magnetization value increased with increasing La content starting with sample, $x = 0.02$; this sample has magnetization value around 30 emu/mole/Oe, then it increased to 40 emu/mole/Oe with $x = 0.04$, moreover, the magnetization value increased to be maximum for the sample with $x = 0.08$, where this composition has a magnetization value around 50 emu/mole/Oe. Then the value of the magnetization start to decrease with the La content, confirming the critical value of the optimization for the magnetic properties, to be $x = 0.08$. The second feature here is the samples undergo the transition from ferromagnetic to paramagnetic around 400 K, the transition shifted to higher temperature with increasing the La content.

In Fig. 3(b) presents the magnetization divided applied field as a function of the temperature for samples with different La-content ($x = 0.02, 0.04, 0.06, 0.08, 0.1$). The measurements have been done during heating after cooling in ZFC (zero field cooled) from room temperature to around 2 K. It can be concluded that the $T_c$ does not change with applied field, the
magnetization value has the maximum for the sample with $x=0.08$. If a comparison between the measurements is made, with and without applied field, it is possible to notice that for all compositions, the magnetization measured in both ZFC and FC modes of applying fields has the same behavior. The only difference here is that the observed drop in the ZFC magnetization versus temperature of the Li$_{0.5-0.5x}$Zn$_x$La$_x$Fe$_{2-0.5x}$O$_4$ below 50K probably arises from a coercive field. In the measurements with the applied field, the field is relatively small ($H=1000$ Oe). Also, the coercive fields are very high, the maximum value is achieved at $x=0.08$ and then decreasing again for $x \geq 0.08$. One can noted here that, in the case of FC the increase of temperature causes a very rapid increase in the flux density causing a pronounced steady of $\chi$. While, in case of ZFC, a slight decrease of $\chi$, with increasing temperature, while the sample with $x=0.1$ shows nearly $\chi$ constant in case FC, then it changes to $x=0.06$ at ZFC. Moreover, from the figure, Curie temperature ($T_c$) decreases with increasing La content. This may be originating from the nonmagnetic nature of La$^{3+}$ ions, which may break linkages between magnetic cations. No maximum value of Curie temperature occurs in the samples studied. This is agreed well with [22,23].

Fig. 4 shows the relation between the reciprocal magnetic susceptibility $\chi$ and the absolute temperature $T$ for different samples with La content ($x$). It is clear the concentration and temperature dependence of ferromagnetic susceptibility $\chi$ per mole of iron atoms. The effect of La content ($x$) on the magnetic susceptibility $\chi$ at a selected temperature Fig. 4(a) shows decreases of $\chi$ to reach a minimum at $x=0.08$ which considers the critical concentration and then increases for $x>0.08$. These results are consistent with the changing of the grain size due to higher ionic radius of La$^{3+}$ (1.13 Å). Fig. 4(b) shows the magnetization curves are shift to lower values as La content increases since the magnetic moment of La$^{3+}$ is smaller than that of Fe$^{3+}$, resulting in the decrease of the A–B interaction. Moreover, the magnetization tends to be saturated at about 5 kOe. The hysteresis loop is clearly at around 40 kOe. This facts indicate that Li-Zn ferrite exhibits ferrimagnetic behavior below room temperature ($T=5$ K). It is thought that the investigated samples, possessing the metastable structure; four coordinated as well as six coordinated Fe$^{3+}$ ions are present in the crystal structure, leading to strong super exchange interaction between Fe$^{3+}$ ions in the tetrahedral and octahedral sites [18].

Fig. 5 provides information about the behavior of the system at low temperature (5 K). The magnetic moments as a function of the external applied magnetic field ranging between 0 and ±5000 Oe were carried out. The $M$ versus $H$ plots of the compounds presented at ZFC in Fig. 5(a)-(e). The graphs of all the concentrations show ferromagnetic samples at low temperature (5 K). It is clearly that the value of maximum magnetization increases as $x$ increases ($0.0 \leq x \leq 0.08$), and decreases systematically as $x$ increases ($0.08 \leq x \leq 0.1$), at temperature of 5 K. The saturation only takes place for samples $x=0.04$, 0.06, 0.08, but the sample with $x=0.08$ shows ferromagnetic behavior and relatively high magnetic dipole moments reached 3. On the other hand, the hysteresis loops of samples 0.1 and 0.02 approached a saturation of M with fields $H=30$ kOe with a smaller coercive fields than samples at 0.06, however they show a relatively small remnant magnetization. Our interpretation is that the samples ($x<0.02, 0.1$) in this case are ferromagnetic, and the double-exchange is behind the ferromagnetic behavior, and the antiferromagnetic contribution, if present at all is very week compared to the double-exchange Fe$^{2+}$–Fe$^{3+}$ mechanism responsible for the ferromagnetic ordering in this system [23].
**Fig. 6** – SEM photographs Li$_{0.5-0.5x}$Zn$_y$La$_x$Fe$_{2.5-0.5x-y}$O$_4$ ($0.02 \leq x \leq 0.1$) and $y = 0.6$.

4. Conclusion

High purity oxides of compositions of Li$_{0.5-0.5x}$Zn$_y$La$_x$Fe$_{2.5-0.5x-y}$O$_4$ ($0.02 \leq x \leq 0.1$) and $y = 0.6$ were prepared using the conventional ceramic technique. The effect of La$^{3+}$-content on the magnetic properties of the Li-Zn-ferrite at low temperature was studied. Adding of R$^{3+}$ ions, because of its large ionic radius, exhibited the grain growth and improve the temperature dependence of $X$ and $M_s$. The saturation magnetization ($M_s$) decreases with increasing La-content, in addition all compositions show soft ferromagnetic in the temperature range studied (2-400 K). Combine study of X-ray, SEM, and IR spectra, confirmed ordered spinel ferrite structure. Fine particle play an important role on controlling the magnetic properties of ferrites.

**Conflicts of Interest**

The authors declare no conflicts of interest.

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