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Enhanced structural and magnetic properties of microwave sintered Li–Ni–Co ferrites prepared by sol–gel method

Nandeibam Nilima[1], M Maisnam[2,†], and Sumitra Phanjoubam[3]

[1] *Department of Physics, Oriental College, Takyel, Imphal-795001, India*
[2] *Department of Physics, NIT Manipur, Langol, Imphal-795004, India*
[3] *Department of Physics, Manipur University, Canchipur, Imphal-795003, India*

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The properties of lithium ferrites are very sensitive to chemical composition, synthesis method, and sintering techniques. Li–Ni–Co ferrites with compositional formula $Li_{0.45-0.5x}Ni_{0.1}Co_xFe_{2.45-0.5x}O_4$, where $0.00 \leq x \leq 0.1$ in steps of 0.02 were prepared by chemical sol–gel method and sintered by microwave sintering technique. The x-ray diffraction patterns confirmed the formation of single phase with spinel structure in all the samples. The structural parameter *viz.* lattice constant, crystallite size, and x-ray density for these samples were studied and compared with those measured from samples of similar composition prepared by the sol–gel method and sintered by conventional sintering technique. Enhancement in the magnetic properties like Curie temperature, hysteresis parameters was observed by employing sol–gel synthesis combined with microwave sintering. The results obtained and mechanisms involved are discussed in the paper.

Keywords: lithium ferrites, sol–gel chemistry, magnetic properties, x-ray diffraction

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1. Introduction

Lithium ferrites are found to be good substitutes of garnets for use in microwave devices such as isolators, circulators, gyrators, and phase shifters. High resistivity, high Curie temperature, a wide range of saturation magnetization, square hysteresis loop behavior, low dielectric and magnetic losses, *etc*. of these ferrites have made them useful functional materials.[1–3] Their properties are greatly influenced by the method of preparation and heating technique, chemical composition, nature, and amount of substituents, *etc*.[3,4] The sol–gel method is a simple, easy, and less time consuming method for synthesizing homogenous ultrafine ferrite powder with good stoichiometry at low temperature; however, there are also problems such as high cost, environmental pollution by nitrate decomposition, and inconvenient mass production.[5–9] And heat treatment of such fine powders by microwave process is expected to yield ferrites of better quality. Microwave sintering has various advantages like rapid and uniform heating, high reaction rate, reduced sintering temperature, thereby, energy and time saving and thus eco-friendly.[10–13] The present work aims to synthesize Li–Ni–Co ferrites by the sol–gel method and then employ microwave and conventional sintering techniques to heat treat the samples with an attempt to make a comparative study of the structural and magnetic properties.

2. Experimental method

$Li_{0.45-0.5x}Ni_{0.1}Co_xFe_{2.45-0.5x}O_4$, nanoparticle ferrites where x ranges from 0.00 to 0.1 in steps of 0.02 were prepared using the chemical sol–gel method. The starting materials were lithium nitrate ($LiNO_3 \cdot 3H_2O$), cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, iron nitrate ($Fe\ (NO_3)_3 \cdot 6H_2O$, and ethylene glycol (all from Merck, Mumbai). The detailed preparation method has been reported elsewhere.[14] The as-prepared ferrite powder was mixed with a small amount of PVA (3% by weight percentage) as a binder and then pressed in the form of pellet by applying a load of 100 kg/cm^2 for 5 min. One set of samples was sintered by conventional resistive sintering at 900 °C for 4 h and another set at 900 °C for 10 min by the microwave sintering technique and subsequently furnace cooled. XRD studies were carried out on the samples using Phillips X-Pert Pro PAN analytical x-ray diffractometer. Various structural parameters like lattice constant, crystallite size, x-ray density, and porosity were determined. The morphology was investigated by using transmission electron microscopy (TEM, JEOL JEM 2100, 200 kV) and scanning electron microscope (SEM, FEI QUANTA- 250) magnetic hysteresis measurements were taken by using a vibrating sample magnetometer (Lakeshore, Model: 7410 series). The Curie temperature was determined using Soohoo's method.[15]

3. Results and discussion

The typical XRD patterns for both the conventional sintered (CS) and microwave sintered (MS) samples are shown in Fig. 1, and the patterns confirmed the formation of single phase with spinel structure without formation of any extra lines showing that there is no impurity present. Various structural properties obtained from the analysis of the XRD data are tabulated in Table 1.

†Corresponding author. E-mail: m_maisnam@yahoo.co.in

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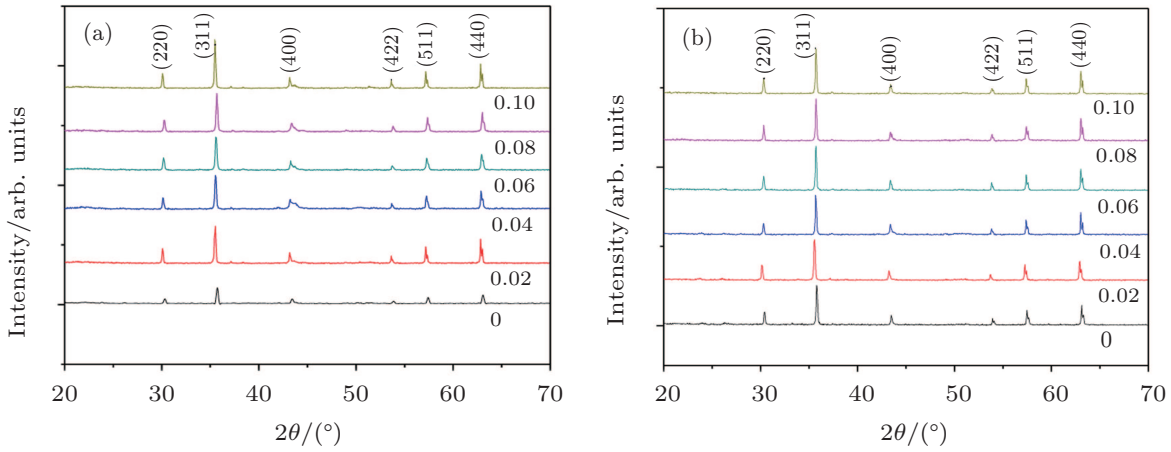


Fig. 1. XRD patterns for $Li_{0.45-0.5x}Ni_{0.1}Co_xFe_{2.45-0.5x}O_4$ ferrites heated by (a) conventional and (b) microwave sintering technique.

Table 1. Structural parameters of $Li_{0.45-0.5x}Ni_{0.1}Co_xFe_{2.45-0.5x}O_4$ nanoferrite heated by conventional and microwave sintering technique.

Co^{2+} content x	Lattice constant a/Å		Crystallite size D/nm		X-ray density d_x/(g/cc)		Porosity P/%	
	CS	MS	CS	MS	CS	MS	CS	MS
0.00	8.329	8.321	30	49	4.823	4.837	15.59	11.97
0.02	8.328	8.333	35	50	4.837	4.813	15.17	10.76
0.04	8.335	8.335	47	52	4.837	4.836	8.47	6.61
0.06	8.354	8.336	49	56	4.817	4.849	8.09	6.94
0.08	8.360	8.336	47	55	4.854	4.866	6.32	6.30
0.10	8.371	8.359	59	56	4.813	4.875	6.81	6.23

For both the sets of samples, the lattice constant shows an increasing trend with the increase of Co^{2+} concentration. Co^{2+} ion being larger in size (ionic radius of 0.82 Å) as compared to Li^+ and Fe^{3+} ions (ionic radii of Li^+ and Fe^{3+} are 0.74 Å and 0.67 Å respectively), its substitution will result in expansion of the unit cell dimension. Hence, an increase of the lattice constant is expected and has been observed in both the sets of samples, implying that Co^{2+} ions are progressively being substituted obeying Vegards law.[16] A comparative study of structural parameters (Table 1) was done and found that the increase in lattice constant is significant in CS samples as compared to MS samples. However, for higher Co^{2+} ion substitutions ($x \geq 0.08$), lattice constant is observed to increase fast with microwave sintering. It is also observed from Table 1 that microwave sintering improves the density significantly and porosity is comparatively reduced. In the conventional sintering technique, heat is generated by the heating element and the thermal energy is absorbed on the surface of the sample and then it is transferred inside the sample via conduction, convection and radiation. Such a process required a long time to sinter the sample which may lead to vaporize lithium and oxygen content, leaving behind intragranular pores that get trapped in the bulk resulting in a reduction of density for the CS samples. While in the case of microwave sintering technique, the sample itself absorbed the microwave energy and transferred it within the sample volume and heating the sample, thereby completing the sintering process in a shorter time and, therefore, has very little chance of materials volatization.[13,17] Hence, higher values of density with reduced porosity in MS samples are expected. The crystallite size was also found to be larger in the microwave sintered samples indicating better crystallization. Microwave lowers the activation energy of sintering kinetics and crystal growth is known to progress comparatively faster.[18] The observed higher densification with reduced porosity in the MS sample has been achieved within ~ 10 minutes of sintering cycle compared to the long 4 hours of CS cycle. This indicates that the MS technique is efficient enough to process the ferrites with enhanced microstructures at a much reduced time.

Typical TEM photographs for the sample with $x = 0.10$ sintered by conventional and microwave sintering are shown in Fig. 2, which show that the particles are spherical in shape and dispersed uniformly. The particle sizes as given by the TEM photographs are found in the range 21 nm–27 nm for CS samples while the value lies in the range 23 nm–33 nm for MS samples.

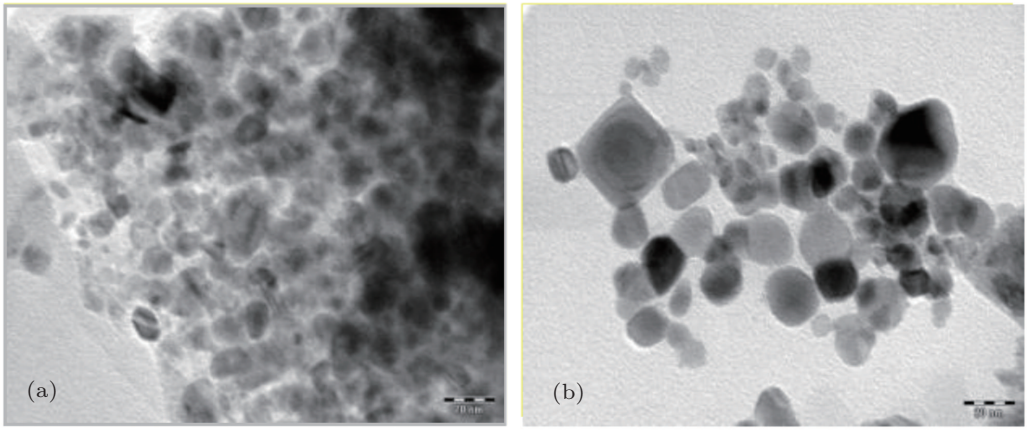


Fig. 2. Typical TEM photograph for the $Li_{0.45-0.5x}Ni_{0.1}Co_xFe_{2.45-0.5x}O_4$ nanoferrite (for $x = 0.10$) heated by (a) conventional, and (b) microwave sintering technique.

Selected area electron diffraction (SAED) patterns for $x = 0.1$ for both the CS and MS samples are shown in Fig. 3 and the appearance of diffraction rings in the pattern indicates that the prepared samples are purely crystalline in nature.[19,20] Typical SEM microphotographs for $x = 0.06$ for both the CS and MS processed samples are shown in Fig. 4, revealing the morphology of the samples. The average grain size of the CS and MS samples lies in the range of 299 nm to 450 nm and 298 nm to 615 nm respectively. The large grain observed may be attributed to the agglomeration of the fine attractive magnetic nano-crystallites due to magnetic cohesion.

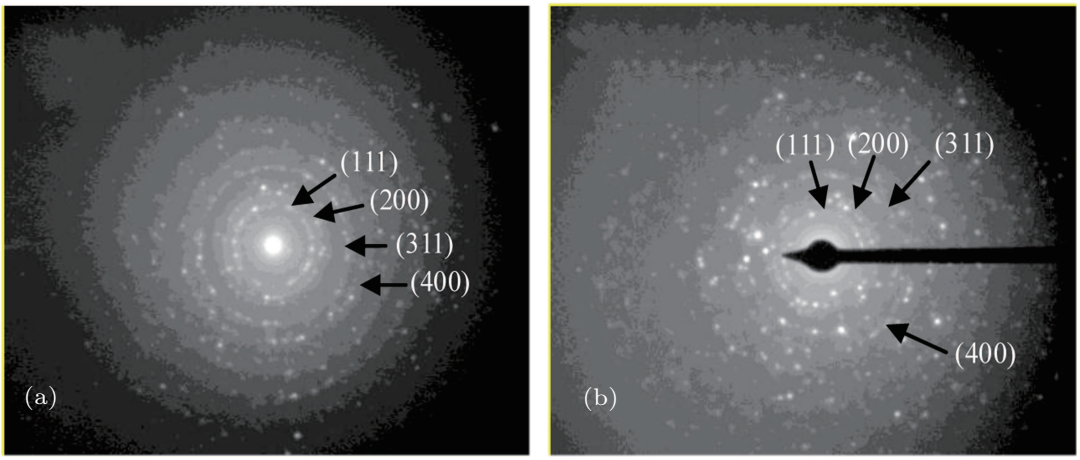


Fig. 3. SAED for the $Li_{0.45-0.5x}Ni_{0.1}Co_xFe_{2.45-0.5x}O_4$ (for $x = 0.10$) nanoferrite heated by (a) conventional, and (b) microwave sintering technique.

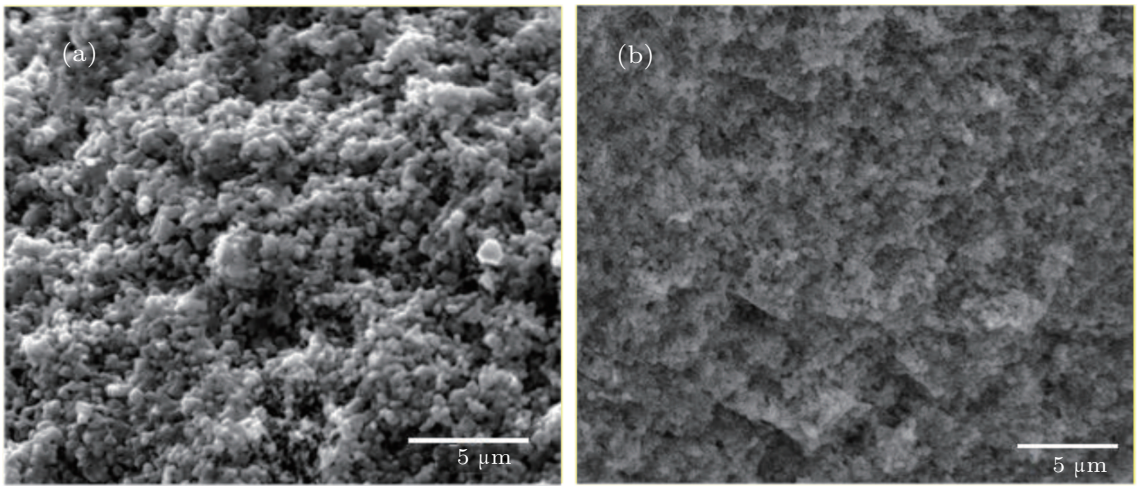


Fig. 4. SEM photograph for the $Li_{0.45-0.5x}Ni_{0.1}Co_xFe_{2.45-0.5x}O_4$ (for $x = 0.06$) nanoferrites heated by (a) conventional and (b) microwave sintering technique.

Table 2. Various magnetic parameters of $Li_{0.45-0.5x}Ni_{0.1}Co_xFe_{2.45-0.5x}O_4$ nanoferrite heated by conventional and microwave sintering technique. The unit 1 Gs = 10^{-4} T.

Co^{2+} content x	Curie temperature T_c/°C		Saturation magnetization M_s/(emu/g)		Remanence M_r/(emu/g)		Coercive force H_c/Gs	
	CS	MS	CS	MS	CS	MS	CS	MS
0.00	629	631	54	62	5.5	6.5	105	121
0.02	624	627	57	63	4.8	5.4	85	116
0.04	619	623	58	66	6.4	4.6	101	112
0.06	617	621	60	67	7.5	6.1	131	166
0.08	616	618	61	67	6.1	5.7	148	145
0.10	609	612	61	64	5.0	7.8	158	210

The Curie temperature of all the samples showed a decreasing trend with progressive Co^{2+} substitution. The decreased Curie temperature can be understood from exchange interaction existing between Fe^{3+} ions and cationic distribution. According to Neel, three types of exchange interaction namely AA, BB, and AB interactions occur between unpaired electrons, out of which AB interaction significantly predominates over the other two.[21] In ferrites, therefore, the Curie temperature is known to depend on the number of active Fe^{3+}_A–O^2–Fe^{3+}_B linkages, which in turn depends on the number of Fe^{3+} ions in the formula unit.[22,23] In spinel ferrites, Ni^{2+} ions are known to occupy the B sites. Low concentrations of Co^{2+} ions are reported to occupy the B sites, while, for higher concentrations, Co^{2+} ions start migrating to A sites also. In the present study, as $x \leq 0.1$, it may be assumed that Co^{2+} ions preferably occupy the B sites.[24–27] Hence the cation distribution may be assumed qualitatively as

$$(\mathrm{Fe})\ [Li_{0.45-0.5x}Ni_{0.1}Co_xFe_{1.45-0.5x}]O_4, \quad (1)$$

where the parenthesis and the square brackets represent tetrahedral A site and octahedral B site respectively. Increase in the concentration of Co^{2+} ions decreases the amount of Fe^{3+} ions in the ferrites, thereby decreasing the number of active Fe^{3+}_A–O^2–Fe^{3+}_B linkages. Hence, the decrease in Curie temperature is expected with the increase in Co^{2+} content.

Curie temperature of the MS samples showed slightly higher value as compared to that of CS samples. This may have been due to the control of loss of lithium by microwave sintering technique. The shorter sintering time in microwave sintering technique may have restrained the evaporation of lithium and oxygen ions. Reduction in the loss of lithium and oxygen ions may control the conversion of Fe^{3+} ions to Fe^{2+} ions,[8] thereby MS samples may possess larger number of active Fe^{3+}_A–O^{2-}–Fe^{3+}_B linkages which determine Curie temperature. Hence, the Curie temperature of MS samples is observed slightly higher compared to CS samples which may indicate higher operating temperature limit.

The plot of magnetization versus applied field, *M*–*H* hysteresis loop for both the CS and MS samples are shown in Fig. 5. Various hysteresis parameter obtained from the loop are tabulated in Table 2.

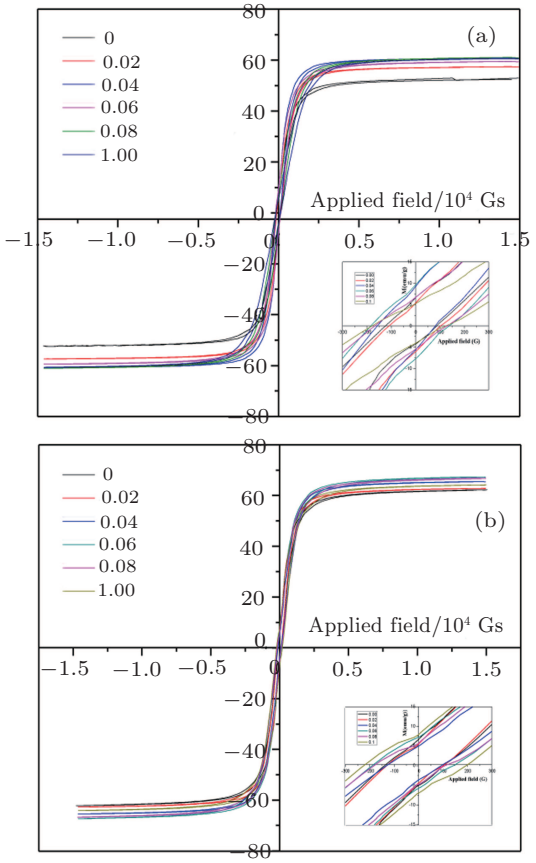


Fig. 5. Room temperature *M*–*H* loop for $Li_{0.45-0.5x}Ni_{0.1}Co_xFe_{2.45-0.5x}O_4$ nanoferrite heated by (a) conventional and (b) microwave sintering technique. The inset is the local enlarged *M*–*H* plot in the range from −300 Gs to 300 Gs.

A slight increase in saturation magnetization for both the samples was observed and this can be explained by Neel's molecular field model.[21] According to Neel, magnetization in spinel ferrites is mainly because of the uncompensated electron spin of the individual ion and the antiparallel alignment of spins in A and B sublattices. Therefore, the saturation magnetization is given by the net magnetic moment of the individual A and B sublattices, *i.e.*, $M_s = M_B - M_A$. Keeping the amount of Ni^{2+} constant, the amount of Li^+, Co^{2+}, and Fe^{3+} ions vary with the substitution level. Li ions is non-magnetic whereas the ions such as Co^{2+}, Ni^{2+}, and Fe^{3+} have their own magnetic moment of 3 μ_B, 2 μ_B, and 5 μ_B respectively. Hence variation in Co^{2+} content influenced the magnetic properties of the materials. Considering cation distribution, the net mag-

netic moment can be written as

$$M_B - M_A = 2(0.1) + 3x + 5(1.45 - x/2) - 5(1.0) = 2.45 + 0.5x. \quad (2)$$

Therefore, substitution of Co^{2+} ions increases the net magnetization and this increases the saturation magnetization.[28] A close observation of the table shows magnetic properties *viz.* saturation magnetization M_s and coercivity H_c to be enhanced in the microwave sintered samples. Microwave sintering enhances reaction process during synthesis; the ferrite processing is expected to be improved in this technique. Spinel phase components in MS samples per unit volume are expected to be higher in MS samples. Therefore, the increase in saturation magnetization may be the better degree of spinel solid phase reaction completion for the MS samples. Excitation of magnetic dipoles due to microwave interaction during processing may contribute to enhanced hysteresis properties as has also been reported by others.[29] Furthermore, the hysteresis parameters of ferrites are known to be dependent on many factors such as stoichiometry, porosity, density, microstructures, exchange magnetization, magnetostriction, stress, anisotropy constant, *etc*.[30] The observed fluctuation in the values of remanence for both the CS and MS samples may be attributed to the interplay of the above factors.

4. Conclusion

Li–Ni–Co ferrite samples with compositional formula $Li_{0.45-0.5x}Ni_{0.1}Co_xFe_{2.45-0.5x}O_4$ were successfully prepared by sol–gel method and sintered using two different sintering techniques, *i.e.*, conventional sintering (CS) and microwave sintering (MS) technique. X-ray diffraction studies confirmed the formation of single phase spinel structure in all the samples. The nanocrystalline nature of ferrites was confirmed by TEM analysis. MS samples were found to possess better densification and improved microstructures. Various magnetic properties like Curie temperature, saturation magnetization and coercivity were observed to be enhanced in the microwave sintered samples.

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