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Processing and properties of cobalt-substituted lithium ferrite in the GHz frequency range

Nutan Gupta, Mukesh C. Dimri, Subhash C. Kashyap*, D.C. Dube

Department of Physics, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India

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Abstract

Polycrystalline cobalt-substituted lithium ferrites with general formula $Li_{0.5-x/2}Co_xFe_{2.5-x/2}O_4$ ($x = 0.0$, 0.2, 0.4 and 0.5) were prepared by a non-conventional citrate precursor method, which is advantageous over conventional (solid state sintering) method because of low temperature (600 °C) processing. Small amounts of Bi_2O_3 (0.5 wt.%) were added to reduce the porosity and dielectric loss tangent at sintering temperatures (1000–1200 °C). The complex magnetic permeability ($\mu' - j\mu''$) and complex dielectric permittivity ($\epsilon' - j\epsilon''$) of cobalt-substituted lithium ferrites were measured in the 8–13 GHz microwave frequency range. The systematic variations of the real and imaginary parts of both permeability and permittivity with frequency and composition have been analyzed. The minimum value of $\epsilon' \sim 11.3$ measured for $x = 0.4$ substituted lithium ferrite is observed for a sample sintered at 1000 °C. The highest values of ϵ' and ϵ'' were observed for samples sintered at 1200 °C. μ' varies between 1.84 and 3.90 for pure and cobalt-substituted lithium ferrite bulk ceramics. The spinel structure of the samples was confirmed by X-ray diffraction (XRD).

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Keywords: Lithium ferrite; Citrate precursor method; Complex permittivity; Complex permeability

1. Introduction

Spinel ferrites have potential applications in electrical components, memory devices and microwave devices over a wide range of frequencies because of their high resistivity and low loss behavior [1–3]. Ease of fabrication, low cost, high Curie temperature and better temperature stability of saturation magnetization of lithium ferrites have made them attractive from commercial point of view and are good substitutes of garnets for microwave devices such as isolators, circulators, gyrators and phase shifters. Lithium ferrite has an important role in microwave latching devices, magnetic switching circuits and can also be used as cathode material in lithium batteries. There are many reports on the effect of magnetic and non-magnetic substitutions on various properties of lithium ferrite [4–7]. At high power levels, the nonlinearities impair ferrite performance in microwave device applications. To avoid microwave power loss for device applications, the incorporation of Co^{2+} ions in lithium ferrites is found very effective. Co^{2+}, being a fast relaxing ion enhances the microwave properties. For microwave applications, dense, defect free and fine grained ferrite materials are required [8]. Several wet chemical methods like co-precipitation, organic precursor method, spray drying, etc. have been used for ferrite preparation [9,10]. In the present work, a wet chemical method, the citrate precursor method, has been used to obtain a homogeneous, fine grained, pure and cobalt-substituted lithium ferrite powder. A small amount of Bi_2O_3 is added to ensure good densification and to minimize the loss of lithium and oxygen [11].

2. Experimental procedure

Polycrystalline samples of $Li_{0.5-x/2}Co_xFe_{2.5-x/2}O_4$ with compositions $x = 0.0$, 0.2, 0.4 and 0.5 were prepared by the

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* Corresponding author. Tel.: +91 11 26591346; fax: +91 11 26581114.
E-mail address: skashyap62@hotmail.com (S.C. Kashyap).

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citrate precursor method. This method avoids the lithium and oxygen volatilization which reduces resistivity and increases microwave losses, is simple and low cost, gives homogeneous, atomic scale mixing of metal ions and provides low temperature ferrite formation. Lithium nitrate (98% Merck, Germany), cobalt nitrate (98%, Merck, India), iron(III) citrate (Merck, Germany) and citric acid (99.5%, Merck, India) were used as starting materials. The experimental procedure to obtain the precursor mixture (transparent in colour) has been described elsewhere [12]. After adding an appropriate amount of ammonium hydroxide solution the precursor mixture was heated (without boiling) with constant stirring to allow water and ammonia to evaporate. The brown colored fluffy mixture, left behind was calcined at 600 °C for 2 h at a slow heating rate (~2 °C/min). Small amounts of bismuth oxide (0.5 wt.%) were added to the ferrite powder obtained. The resulting ferrite powder was homogeneous. Polyvinyl alcohol (2 wt.%) in aqueous solution was added to the calcined powder to act as binder and finally ground to dryness. The powder mixture was pressed into pellets (diameter 15.00 mm and thickness 1.25 mm) by applying a load of 10 tonnes. The samples were sintered in air for 1 h at three different sintering temperatures: 1000, 1100 and 1200 °C and subsequently furnace cooled. The heating rate was kept 2.5 °C/min. The phase identification of the samples was done by X-ray diffraction (XRD) analysis (Rigaku Geiger Flex 3 kW diffractometer using Cu Kα source) and their microstructure was determined by scanning electron microscopy (Cambridge Stereo Scan-360 SEM).

In the microwave frequency region, the cavity-perturbation is used for the measurement of complex dielectric permittivity and magnetic permeability [13,14]. This method offers the advantage of high sensitivity and requires a small quantity of sample. As dispersive terms of a cavity are related to its resonance frequencies and dissipative terms to its quality factors (‘Q’ values), by an appropriate choice of cavity mode the resulting change in resonant frequency and Q values can be used to calculate the real and imaginary parts of dielectric permittivity and magnetic permeability. The complex magnetic permeability ($\mu' - j\mu''$) and complex dielectric permittivity ($\epsilon' - j\epsilon''$) of cobalt-substituted lithium ferrites were measured in the microwave frequency range (8–13 GHz) by employing the cavity-perturbation method.

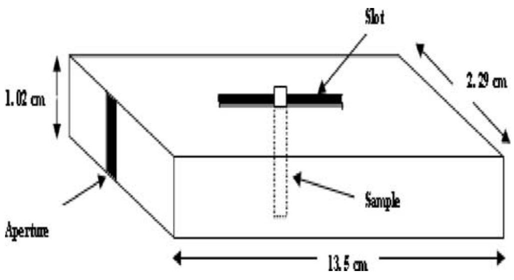

Fig. 1. Rectangular resonator cavity with dimensions L = 13.5 cm, a = 2.29 cm, b = 1.02 cm. Slot is 3 mm × 1.2 mm and the width of the aperture is 2.5 mm.

Shift in the resonance frequencies and quality factors (Qs) were measured by connecting the rectangular cavity having a thin slot (to facilitate sample insertion) ~4 cm in length and 1.2 mm in width to the HP Network Analyzer 8719 ES. The rectangular resonator cavity with dimensions L = 13.5 cm, a = 2.29 cm, b = 1.02 cm and slot is 3 mm × 1.2 mm and aperture width of 2.5 mm is shown in Fig. 1. Thus the corresponding values of ϵ', ϵ'', μ' and μ'' were calculated at microwave frequencies (8–13 GHz) [15].

3. Results and discussion

The X-ray diffractograms of pure and cobalt-substituted lithium ferrite pellets of compositions x = 0.0, 0.2, 0.4 and 0.5 and sintered at 1000 °C are shown in Fig. 2. All patterns show diffraction lines corresponding to the cubic spinel structure with no extra lines, indicating the formation of a single phase. The values of lattice parameter ‘a’ calculated for different samples having x = 0.0, 0.2, 0.4 and 0.5 were found to be 8.328, 8.360, 8.398 and 8.416 Å, respectively. It may be noticed that the lattice parameter (a) increases almost linearly with the increase in Co^{2+} content. This is understandable, as the radius of Co^{2+} (0.82 Å) is larger than that of Li^{1+} (0.74 Å) and Fe^{3+} (0.645 Å) [16]. The scanning electron microphotographs of lithium ferrite samples (x = 0.0) sintered at various temperatures 1000, 1100 and 1200 °C for 1 h are shown in Fig. 3. As can be seen, there is an increase in grain size with increase in sintering temperature. The average grain size of the lithium ferrite sample sintered at 1000, 1100 and 1200 °C is observed to be 1, 1.4 and 6.5 μm, respectively. These values are much smaller than the values (10–18 μm) reported for lithium ferrite samples prepared by the conventional (solid state

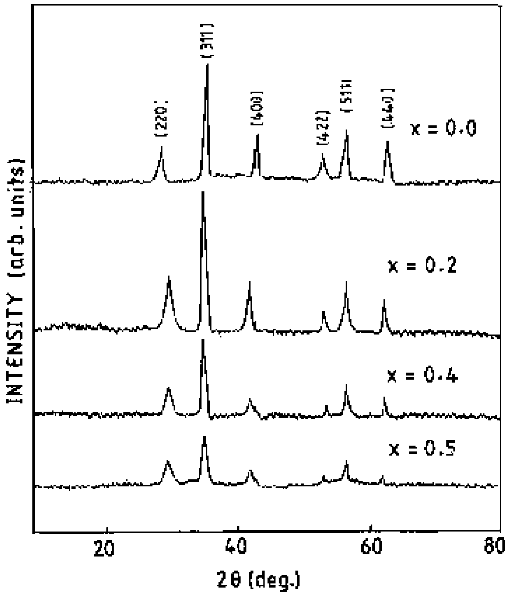

Fig. 2. XRD patterns of pure and cobalt-substituted lithium ferrite pellets of compositions x = 0.0, 0.2, 0.4 and 0.5 and sintered at 1000 °C.

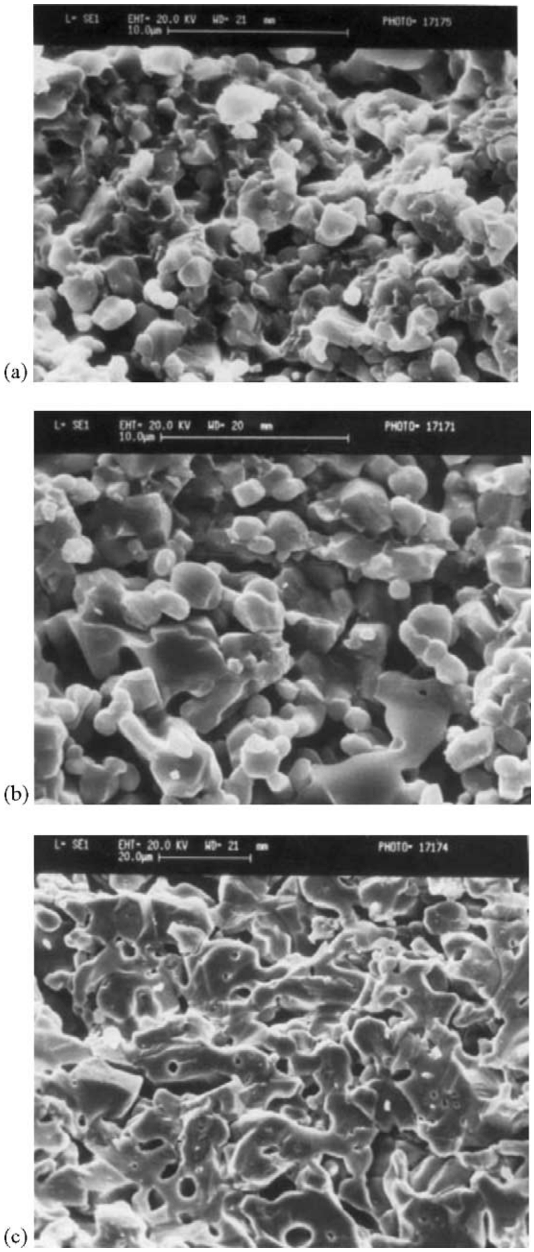

Fig. 3. Scanning electron microphotographs of lithium ferrite (a) sintered at 1000 °C (b) sintered at 1100 °C and (c) sintered at 1200 °C.

sintering) method [17]. Small amounts of bismuth oxide (0.5 wt.%) were added to the calcined ferrite powder obtained to reduce the porosity and dielectric loss tangent at sintering temperatures (1000–1200 °C). In dense materials prepared in this way Bi_2O_3 segregates at grain boundaries and the grains consist of only the basic structure. Sintering at high temperatures (1000–1200 °C) converts a fraction of Fe^{3+} into Fe^{2+} ions due to loss of oxygen and lithium. The presence of small amount of Bi_2O_3 in the calcined powders retains higher fraction of Fe^{3+}, possibly due to smaller loss of lithium. In the case of pure lithium ferrite, the number of ferrous ions is maximum, and hence, it is quite possible for these ions to polarize to the maximum extent.

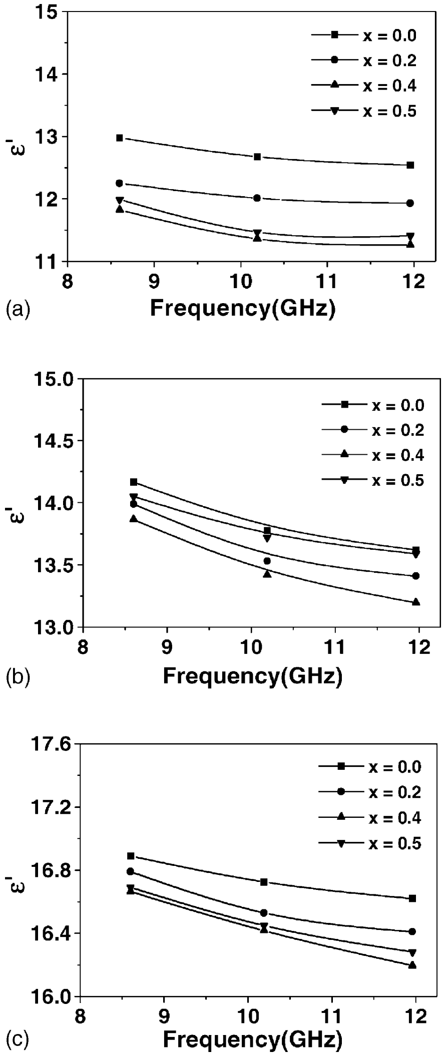

Fig. 4. The variation of the real part of permittivity (ϵ') as a function of frequency (GHz) of $Li_{0.5-x/2}Co_xFe_{2.5-x/2}O_4$ (a) sintered at 1000 °C (b) sintered at 1100 °C and (c) sintered at 1200 °C.

The variation of the real part of the complex dielectric permittivity (ϵ') of polycrystalline pure and cobalt-substituted lithium ferrites sintered at 1000–1200 °C as a function of frequency (GHz) is shown in Fig. 4. The value of the real part of complex dielectric constant (ϵ') is found to decrease with increasing frequency 8.6–11.96 GHz, which shows a normal dielectric behavior of spinel ferrites. As the frequency of the microwave field increases beyond a certain frequency the electronic exchange between Fe^{3+} and Fe^{2+} cannot follow the frequency of the alternating field, thus resulting in gradual decrease in the dielectric constant. The value of the real part of the complex dielectric constant is dependent on composition as well as sintering temperature. The value of the real part of the complex dielectric constant is found to increase with increasing sintering temperature 1000–1200 °C. The observed higher values of ϵ' for pure and cobalt-substituted lithium ferrite might be due to the presence of an higher number of Fe^{2+} at elevated sintering temperatures. High ϵ' values are significant from the view point of size and weight considerations of the microwave device. The value of real part of complex dielectric constant is found to decrease with increasing cobalt content. This may be due to the fact, that ferrites with cobalt content are reported to exhibit greater structural perfection due to the increased reactivity of materials during sintering at high temperatures and Co^{2+}, fast relaxing ions being stabilized in octahedral sites. As cobalt content is increased, it is seen that the number of ferrous ions on the octahedral sites to be polarized decreases, resulting in a continuous decrease of the dielectric constant. The minimum value of ϵ' for composition $x = 0.4$ is observed at any sintering temperature and at any frequency. This might be attributed to the presence of Fe^{2+} to a lower extent in this composition. The variation of the imaginary part of the dielectric permittivity (ϵ'') as a function of frequency (GHz) for samples sintered at 1000–1200 °C is shown in Fig. 5. The values of ϵ'' are found to vary in the range of .0246–.0495 with the sintering temperature 1000–1200 °C and also found to decrease with frequency. The highest value of ϵ'' is measured at a sintering temperature of 1200 °C, which can be explained on the basis that these samples have maximum number of Fe^{2+} ions, which enhance hopping mechanism between Fe^{2+} and Fe^{3+} ions present on equivalent crystallographic sites in the structure, which is responsible for maximum polarization.

The real part of permeability (μ') as a function of frequency (GHz) of samples sintered at 1000–1200 °C is shown in Fig. 6. The real part of permeability varies between 1.84 and 3.90 for pure and cobalt-substituted lithium ferrite bulk ceramics. The variation in the permeability spectra is attributed to domain wall displacement and spin rotation at microwave frequencies. According to Snoek's relation, $\mu' f_r$ = constant, where f_r represents the resonance frequency. It indicates the higher values of μ', the lower value of resonance. Thus, the higher μ' values observed in this case

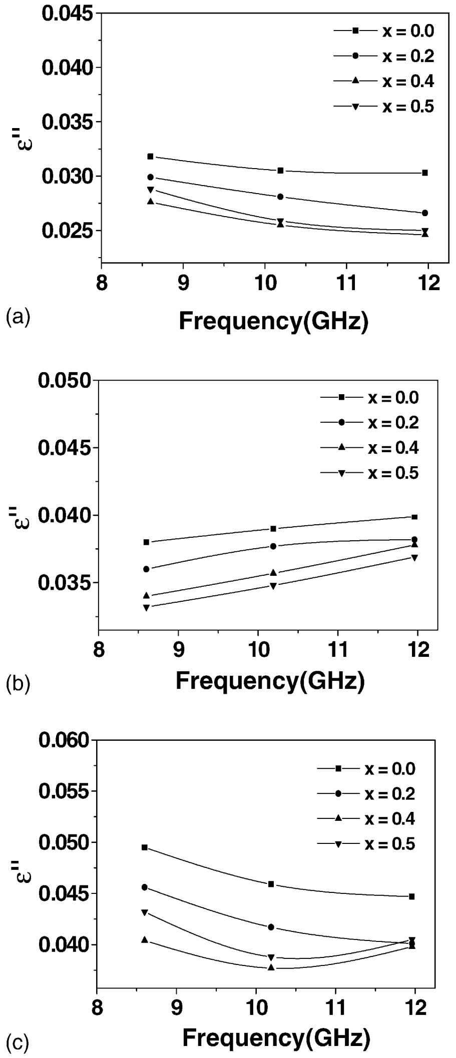

Fig. 5. The variation of the imaginary part of permittivity (ϵ'') as a function of frequency (GHz) of $Li_{0.5-x/2}Co_xFe_{2.5-x/2}O_4$ (a) sintered at 1000 °C (b) sintered at 1100 °C and (c) sintered at 1200 °C.

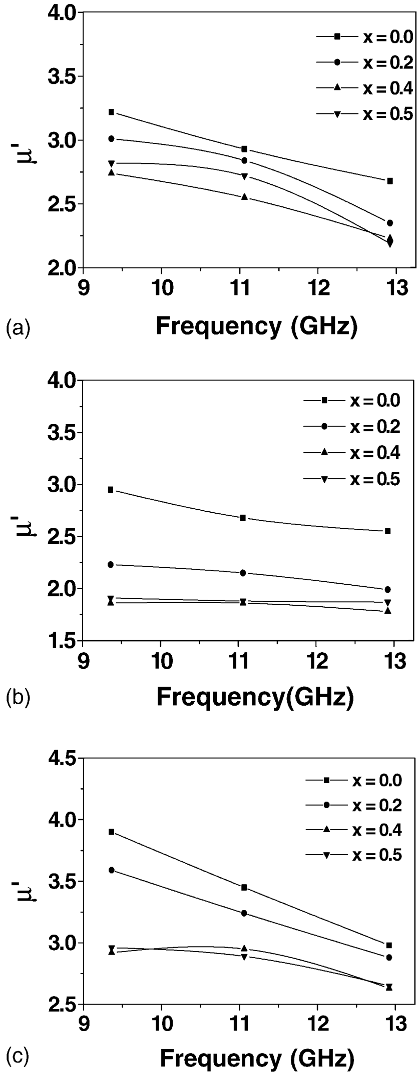

Fig. 6. The variation of the real part of permeability (μ') as a function of frequency (GHz) of $Li_{0.5-x/2}Co_xFe_{2.5-x/2}O_4$ (a) sintered at 1000 °C (b) sintered at 1100 °C and (c) sintered at 1200 °C.

appear to be the post resonance values. The observed increase of μ' with sintering temperature can be attributed to the increased grain size of samples, which facilitates the motion of spins as the number of pores which impede the wall motion are reduced. The increase in the sintering temperature also decreases magnetic anisotropy and crystal anisotropy, which reduce the hindrance to the movement of the domain walls resulting thereby in the increased value of μ'. The imaginary part of permeability (μ'') as a function of frequency (GHz) of samples sintered at 1000–1200 °C is shown in Fig. 7. The permeability loss arises due to lag between the magnetization and applied alternating field. μ'' values are also observed to decrease with the applied frequency exhibiting a small peak at 11.06 GHz, which might be due to the natural magnetic resonance phenomenon implying magnetic relaxation frequency to be directly correlated to morphology. The smaller grain size obtained as a result of citrate processing also results in reduction of domain wall damping which also contributes to the lowering of the magnetic loss factor. In the previous work, no data are available on the permittivity and permeability of cobalt-substituted lithium ferrite samples measured in the GHz range. The dielectric constant and dielectric losses for the samples prepared by a standard ceramic method in the lower frequency range (100 Hz–1 MHz) have been previously reported [5]. In the present work, we have reported that the pure and cobalt-substituted lithium ferrites prepared by citrate precursor method have lower dielectric and magnetic losses in the GHz frequency range. The reduction results because of the appropriate control of composition and microstructure, an asset for the high frequency applications of these ferrites.

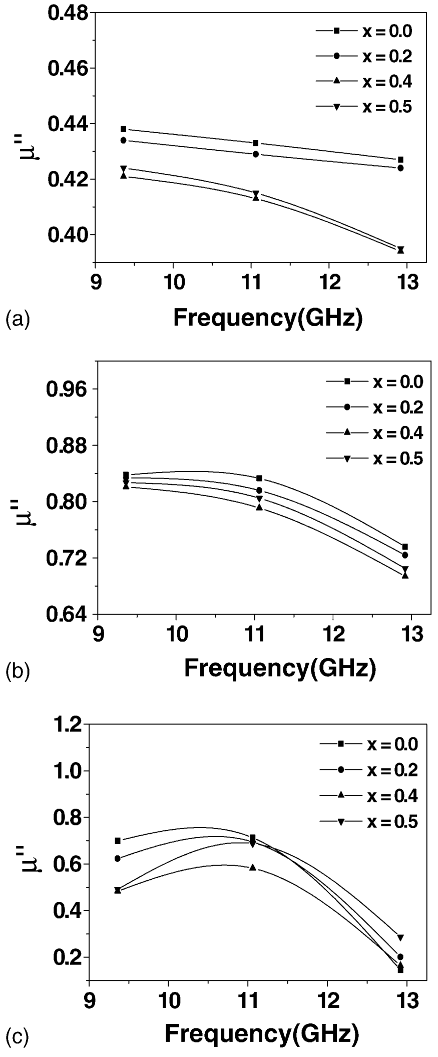

Fig. 7. The variation of the imaginary part of permeability (μ'') as a function of frequency (GHz) of $Li_{0.5-x/2}Co_xFe_{2.5-x/2}O_4$ (a) sintered at 1000 °C (b) sintered at 1100 °C and (c) sintered at 1200 °C.

4. Conclusions

The present work shows that pure and cobalt-substituted lithium ferrites prepared by a non-conventional citrate precursor method have significantly lower values of permittivity and permeability in the microwave frequency region. This reduction in the losses, which makes these ferrites suitable for higher frequency application, can be attributed to stoichiometric composition, purity and improved microstructure (smaller grain size) obtained by the citrate precursor method. The minimum value of $\epsilon' \sim 11.3$ for $x = 0.4$ is observed for the sample sintered at 1000 °C. This might be due to the maximum porosity (14%) in this composition. The values of ϵ' and ϵ'' are found to be maximum for the samples sintered at 1200 °C. Higher values of the real and imaginary part of complex dielectric permittivity are expected due to the increase in the hopping mechanism between Fe^{2+} and Fe^{3+} ions present on equivalent crystallographic sites in the structure of lithium ferrite, which is responsible for maximum polarization.

References

[1] Ernst Schloeman, Advances in ferrite microwave materials and devices, J. Magn. Magn. Mater. 209 (2000) 15.

[2] S.-H. Kang, H.-I. Yoo, Nonstoichiometry (δ) and high temperature thermodynamic properties of $(Mg_{0.22}Mn_{0.07}Fe_{0.71})_{3-\delta}O_4$ ferrite spinel, J. Solid State Chem. 145 (1999) 276.

[3] M. Abe, J. Kuroda, M. Matsumoto, Granular composites containing "micro-onions," permeability and permittivity calculated for application to microwave absorbers, J. Appl. Phys. 91 (10) (2002) 7373.

[4] B.K. Kunar, Effect of the strong relaxor cobalt on the parallel and perpendicular pumping spin-wave instability threshold of LiTi ferrites, J. Magn. Magn. Mater. 163 (1996) 164.

[5] S.C. Watawe, B.D. Sarwade, S.S. Bellad, B.D. Sutar, B.K. Chougule, Micro-structure, frequency and temperature-dependent dielectric properties of cobalt-substituted lithium ferrites, J. Magn. Magn. Mater. 214 (1–2) (2000) 55.

[6] Y.C. Venudhar, K.S. Mohan, Dielectric behavior of lithium–cobalt mixed ferrites, Mater. Lett. 54 (2002) 135.

[7] S.A. Jadhav, Magnetic properties of Zn-substituted Li–Cu ferrites, J. Magn. Magn. Mater. 224 (2001) 167.

[8] M. Pardavi-Horvath, Microwave applications of soft ferrites, J. Magn. Magn. Mater. 215–216 (2000) 171.
[9] B.K. Das, Preparation and characterization of materials, Academic Press Inc., 1981.
[10] D.W. Johnson, B.B. Ghate, in: F.F.Y. Wang (Ed.), in: Proceedings of the International Conference on Ferrites ICF-4, San Francisco, 1984, vol. 27, American Ceramic Society, Columbus, Ohio, 1985.
[11] R. Lalshram, S. Phanjoubam, H.N.K. Sharma, C. Prakash, Electrical and magnetic studies of the spinel system $\mathrm{Li}_{0.5+t}\mathrm{Cr}_x\mathrm{Sb}_t\mathrm{Fe}_{2.5-x-2t}\mathrm{O}_4$, J. Phys. D: Appl. Phys. 32 (1999) 2151.
[12] A. Verma, T.C. Goel, R.G. Mendiratta, R.G. Gupta, High-resistivity nickel–zinc ferrites by the citrate precursor method, J. Magn. Magn. Mater. 192 (2) (1999) 271.
[13] V.R. Murthy, R. Raman, A method for the evaluation of microwave dielectric and magnetic parameters using cavity perturbation technique, Solid State Commun. 70 (8) (1989) 847–850.
[14] R.G. Carter, Accuracy of microwave cavity perturbation measurements, IEEE Trans. Microwave Theory Tech. 49 (5) (2001) 918–923.
[15] A. Verma, A.K. Saxena, D.C. Dube, Microwave permittivity and permeability of ferrite-polymer thick films, J. Magn. Magn. Mater. 263 (1–2) (2003) 228–234.
[16] F.F.Y. Wang, Treatise Mater. Sci. Technol. 2 (1973) 280.
[17] E. Bermejo, T. Le Mercier, M. Quarton, Microstructure and physicochemical studies of pure and zinc-substituted lithium ferrites sintered above 1000 °C, J. Am. Ceram. Soc. 78 (2) (1995) 365–368.