

# Structural Properties of Antimony Substituted Lithium Ferrites Sintered At High Temperature

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**Abstract**— Antimony substituted lithium ferrites with compositional formula  $[\text{Li}_{0.5+x} \text{Sb}_x \text{Fe}_{2.5-2x}] \text{O}_4$  (where  $x = 0.0$  to  $0.5$  insteps of  $0.1$ ) were prepared under standard ceramic method. The bulk and theoretical densities were determined. Bulk density is decreasing up to  $x=0.3$  then increases with gradual increasing the concentration. Similarly theoretical density ( $d_x$ ) decreasing up to  $x=0.3$  and then increases. From X-ray studies the spinel structure and belonging  $Fd\bar{3}m$  space group is confirmed. The lattice parameter was found to be decreases up to  $x=0.3$  then it increases with increase in antimony substituent concentration. The other parameters like Oxygen positional parameters, tetrahedral and Octahedral bond lengths, tetrahedral edge, shared and unshared octahedral edge lengths were calculated and found to be increase with substituent concentration except for  $x=0.3$  samples.

**Key words:** Antimony, Lithium Ferrites, Soft Ferrites

## I. INTRODUCTION

Lithium ferrites belongs to the category of soft ferrites. It has more advantages than other ferrites due to highest Curie temperature, excellent rectangular loop characteristics, high resistivity, low eddy current losses, low dielectric loss and high Neel temperatures, superior temperature stability of saturation magnetization, low intrinsic line width and low magnetic losses. Dielectric properties resemble with those of microwave ferrites. Properties rapidly changes with variation in composition [1-3]. They have excellent flat profile of permeability at high frequencies along with high dielectric constant. In addition to the ease of fabrication and low cost they offer better performance over other ferrites.

Owing to their physical properties lithium ferrites have high potential applications in electrical, magnetic, and microwave components such as circulators, Phase shifters, isolators, filters, oscillators, gyrators and micro wave latching devices. They also have applications as core materials of inductors, transformers, as memory devices in computers, cathode material in rechargeable lithium batteries etc. [4-5].

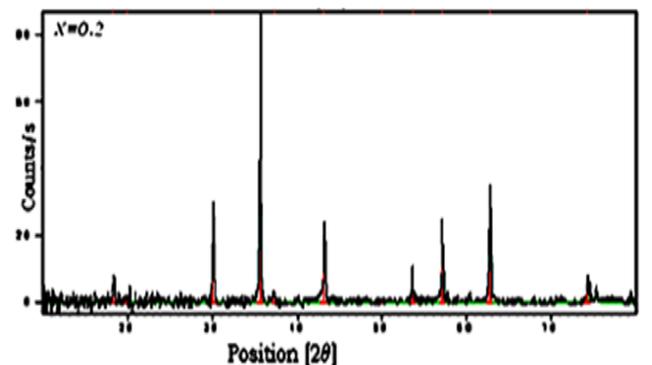
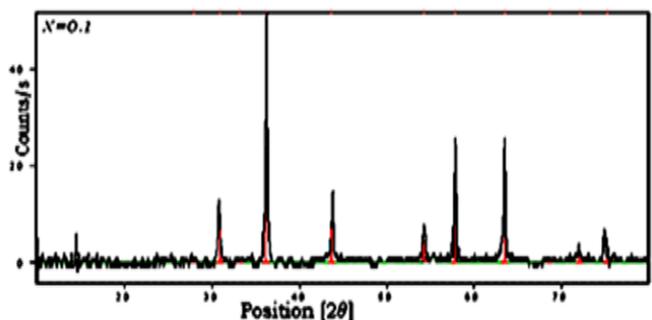
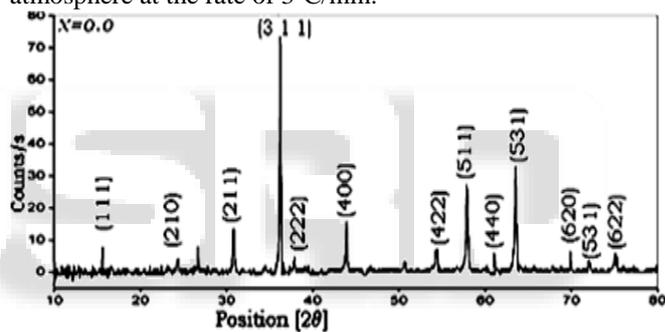
The structure of lithium ferrites is very interesting.  $[\text{Li}_{0.5}\text{Fe}_{2.5}]\text{O}_4$  is an inverse spinel with the  $\text{Li}^{1+}$  and three – fifths of the  $\text{Fe}^{3+}$  ions occupying the octahedral B sites of the cubic spinel structure of the general formula  $\text{AB}_2\text{O}_4$  [6]. Since the number of ferric ions on A and B sites is unequal the magnetization of the sample is given by the difference in the magnetic moments of ions on A and B sites. Consequently, lithium ferrite possesses a higher Curie temperature than other spinel ferrites [7] and other advantages suitable for applications.

The present paper discusses the variation of lattice constants, density, porosity, grain diameter and other structural parameters with substituent concentration. The lattice constant values give the information on the bond

lengths which determine the exchange interactions and chemical interactions

## II. EXPERIMENTAL DETAILS

The ferrite samples with compositional formula  $[\text{Li}_{0.5+x} \text{Sb}_x \text{Fe}_{2.5-2x}] \text{O}_4$  (where  $x = 0.0, 0.1, 0.2, 0.3, 0.4$  and  $0.5$ ) were prepared by conventional standard ceramic method. The appropriate proportions of  $\text{Li}_2\text{CO}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$  were taken and thoroughly mixed in an agate mortar in the presence of methanol. The dried mixture was pre-sintered at  $625^\circ\text{C}$  for 4 hrs. The related powder was ground again and granulated using a small amount of PVA binder. Finally granulated powder was compressed uniaxial under pressure of  $5 \text{ tones/cm}^2$  in a stainless steel die to make pellets and the samples were sintered at  $1200^\circ\text{C}$  for 4hrs for good densification. The samples were cooled in the furnace in air atmosphere at the rate of  $3^\circ\text{C/min}$ .



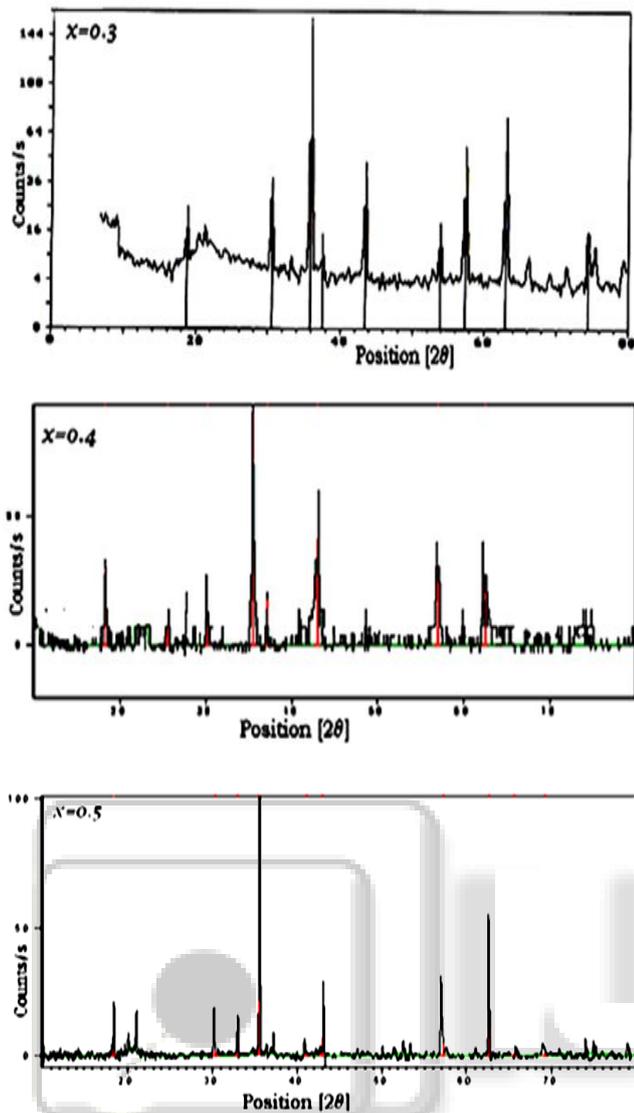


Fig. 1: X-ray diffraction patterns of  $[(Li_{0.5+x}Sb_xFe_{2.5-2x})O_4]$  ferrites, where 'x' varies from 0.00 to 0.5 (X-ray diffractometer it was corresponding to  $x=0.3$  and was recorded using a different x-ray diffractometer)

Due to sintering at  $1200^\circ C$  lithium volatility occurs as a result  $Fe^{2+}$  ions exists [8]. Some of the properties are more attractive sintering at sintering at  $1200^\circ C$  than sintered at  $1000^\circ C$  [9-11].

Theoretical density ( $d_x$ ) of the samples were calculated by using formula

$$(d_x) = \frac{8M}{Na^3} \text{ gm/cm}^3 \quad [12] \quad (1.1)$$

Where

$a$  = Lattice Parameter

8 = Number of molecules in a unit cell of a spinel lattice

$M$  = molecular weight in gram mole of the spinel

$N$  = Avogadro number ( $6.0225 \times 10^{23}$  atom/mole).

The bulk density ( $d_{ob}$ ) of the samples was measured through the Archimedes principle. The lattice parameter 'a' of the samples was determined using PHILIPS (X'pert: Japan) diffractometer in the range between  $15^\circ$  to  $80^\circ$  at room temperature. The  $Cu-K\alpha$  radiation was used and scanning rate was  $3^\circ$ /minute.

### III. RESULTS AND DISCUSSION

The bulk density ( $d_{ob}$ ) is found to decrease up to  $x=0.3$  then it increases with increasing concentration. The observed bulk density of  $4.692 \text{ gm/cm}^3$  for the basic ( $x=0.0$ ) ferrite is in close agreement with the reported value [13]. When the molecular weight increases with increasing concentration of antimony, the density decreases and this can be explained on the basis of decreasing intermolecular forces. This can be understood in terms of sintering. If the sintering temperature is below  $1200^\circ C$  the densification decreases as the value of 'x' increases at high concentration the samples are rendered powder into powder form. From the above-mentioned formula 1.1, lattice constant is inversely proportional to the density. This can be attributed to the densification of the material and depends on the sintering, rate of cooling and heating, furnace atmosphere etc.. The X-ray density is found to exhibit higher value when compared with its bulk density for all samples.

S.No	Substituent	Lattice	Bulk	X-ray	Porosity
	Concen.	parameter	density	density	
	(X)	(a)	( $d_{ob}$ )	( $d_x$ )	
		$\text{gm/cm}^3$	$\text{gm/cm}^3$	%	
1	0.0	8.3313	4.6924	4.7560	1.3
2	0.1	8.3697	4.3742	4.7293	7.5
3	0.2	8.3869	4.3740	4.7386	7.7
4	0.3	8.3649	4.3618	4.8162	9.4
5	0.4	8.4018	4.5265	4.7895	5.5
6	0.5	8.4400	4.5749	4.7623	3.9

Table 1: Variation of lattice parameter (a), X- ray density ( $d_x$ ), experimental density ( $d_{ob}$ ) along with porosity of the ferrites as a function of antimony (x)

The value of theoretical density ( $d_x$ ) is  $4.7560 \text{ gm/cm}^3$  is in good agreement with reported value of  $4.7829 \text{ gm/cm}^3$  [14]. The X-ray density decreases at  $x=0.1$  then increase upto  $x=0.3$  and further increases with continuous increasing concentration of antimony. The variation between these can be related to the porosity differences in materials. Bulk and theoretical/X-ray densities are listed in Table 1.

It is observed porosity ranges varied from 1.3% to 9.4%. Porosity increases from  $x=0.0$  to  $x = 0.3$  then decreases. Lower porosity is required for good quality ferrites material since larger porosity affects physical properties of the material. High valancy cations create cation vacancies, microvoids and bulk diffusion of cations contribute to the increase in percentage of porosity. Generally percentage of porosity is approximately 10 [15]. Since the charge balance is affected by the creation of vacancies, the porosity is found to be more for these ferrites which have high valancy cations as substituents.

From X-ray diffractometer, the lattice parameter was calculated and is in good agreement for  $x=0.0$  with standard JCPDS data card number 72-1911.

Some of the typical spectra are shown in the Fig. 1. The patterns of all the samples exhibited lines corresponding to single phase spinel structure for  $Sb^{5+}$  substituted lithium ferrites. The important peaks of planes (111), (311), (222), (400), (422), (511), (440) and (531) confirm the presence of single phase with face-centered cubic structure [16].

The obtained lattice constant (8.3313 Å) is in good agreement with the reported values (8.316 Å) [14,17-18] of basic ferrite. The values of lattice constant (a) are computed

using the standard extrapolation method (Nelson-Riley function) [19] with error error  $\pm 0.0019$  Å.

S.No	Substituent Conc.	Oxygen Positional parameters	Tet.hedral bond length	Oct. hedral bond length	Tet. edge	Shared oct.hedral edge length	Unshared oct.hedral edge length
	(X)	(Å)	(Å)	(Å)	(Å)	(Å)	(Å)
1	0.0	0.2600	3.6076	6.8290	5.8911	11.7820	6.9079
2	0.1	0.2602	3.6242	6.8605	5.9183	11.8365	6.9398
3	0.2	0.2604	3.6316	6.8746	5.9304	11.8608	6.9541
4	0.3	0.2606	3.6217	6.8558	5.9142	11.8285	6.9351
5	0.4	0.2608	3.6381	6.8868	5.9410	11.8819	6.9664
6	0.5	0.2610	3.6546	6.9181	5.9680	11.9359	6.9981

Table 2: Oxygen positional parameters, tetra hedral, Octa hedral bond lengths, tetra hedral edge, shared and unshared octahedral edge of Li-sb ferrites as a function of substituent concentration.

The lattice parameter (a) values of the basic and substituted ferrites are given in the table 1. It shows that the compositional variation of lattice constant is increasing with increasing of antimony concentrations. The ionic radius of  $Sb^{5+}$  (0.62Å) is smaller than the  $Fe^{3+}$  (0.64Å). So it is expected that the lattice constant decreases with the increase of 'x'. Contrary to this, in the present studies that the lattice constant increases with the increase of 'x' except x= 0.3.

lengths.  $d_{AE}$ ,  $d_{BE}$  and  $d_{BEu}$  are the tetra hedral edge, shared and unshared octa hedral edge lengths. From the table 2 the oxygen parameters 'u' of antimony substituted lithium ferrites increases. All the  $d_{AL}$ ,  $d_{AL}$ ,  $d_{AE}$ ,  $d_{BE}$  and  $d_{BEu}$  values are increased except at x= 0.3 where they decreased and then increased. This is attributed to the fact that at x=0.3 lattice parameter is decreases.

One factor which would influence this behavior is the higher charge of substituent's ions. This can be explained on the basis that ionic radius of  $Li^{1+}$  (0.68 Å) is greater than ionic radius of  $Fe^{3+}$  (0.64 Å) which it replaces at A site. The  $Sb^{5+}$  ions seems to replace the  $Fe^{3+}$  at B site. When  $Li^{1+}$  is added, the  $Fe^{3+}$  moves from A site to B site. Therefore, lattice constant increases. The similar behavior with  $Sb^{5+}$  was observed from earlier [20-21].

#### IV. CONCLUSION

Further this can be explained as, lithium ferrites exist in two different crystalline forms [22]. The phase with FCC inverse spinel structure and space group  $P4_332$  in which all  $Li^{1+}$  ions and 3/5 of all  $Fe^{3+}$  ions occupy the octahedral B- sites in an ordered fashion whereas the remaining  $Fe^{3+}$  ions occupy the tetrahedral A -sites. The  $\beta$ -phase is a similar structure except that  $Li^{1+}$  and  $Fe^{3+}$  ions are randomly distributed in the octahedral interstices and space group is  $Fd\bar{3}m$ . Therefore, it is supports the above observations of increasing lattice constant as  $Li^{1+}$  replaces  $Fe^{3+}$ .

The bulk and X-ray densities were calculated and the differences between them were discussed. The bulk density is found to decrease up to x=0.3 and then increases. The X-ray densities were calculated and found to decrease upto x=0.1 and then it increases upto x=0.3 from where it increases with continuous increasing of antimony concentration. The changes in density with substituent concentration are attributed to the changes in sintering. The differences between the bulk density and theoretical densities are attributed to porosity. Porosity of the samples was calculated and found to be increasing from 1.3 to 9.4%. X- ray diffraction pattern of all the samples confirm single phase spinel structure without any evidence of unreacted ingredients. X- ray diffraction pattern of lithium ferrites confirm the  $\beta$ - phase with space group  $Fd\bar{3}m$ . The lattice constant is found to increase with increasing Sb substituent concentration except x=0.3 where it decreases. Oxygen positional parameters, tetrahedral and octahedral bond lengths, tetrahedral edge, shared and un shared octahedral edge lengths been evaluated and these are found to be increasing except x=0.3 sample where they decrease slightly.

Using the lattice constant 'a', we can calculate some other structural parameters also i.e. inter ionic distances, tetrahedral and octahedral bond lengths etc. have been computed and presented in the Table 2 with the following formulae [21,23-24]:

#### REFERENCES

$$d_{AL} = a\sqrt{3} \left[ u - \frac{1}{4} \right] \quad (2.1)$$

$$d_{BL} = a \left( 3u^2 - \frac{11}{4}u + \frac{43}{64} \right)^{\frac{1}{2}} \quad (2.2)$$

$$d_{AE} = a\sqrt{2} \left( 2u - \frac{1}{2} \right) \quad (2.3)$$

$$d_{BE} = a\sqrt{2} (1 - 2u) \quad (2.4)$$

$$d_{BEu} = a \left( 4u^2 - 3u + \frac{11}{16} \right)^{1/2} \quad (2.4)$$

Where 'u' is the oxygen positional parameter values are calculated [25-26] and listed in the Table 2.  $d_{AL}$  and  $d_{BL}$  represent the tetra hedral and octahedral bond

- [1] J. S. Baijal, Sumitra Phanjouam, D. Kothari, C. Prakash, P.Kishan, "Hyperfine interactions and magnetic studies of Li-Mg ferrites" Solid State Commun., Vol. 83 March 1992 pp. 679-682.
- [2] P. B. Braun, Nature, "A Superstructure in Spinel" Vol. 170 Dec. 1952, pp. 1123-1123.
- [3] K. B. Modi, J. D. Gajera, M. C. Chhanbar, K. G. Sailaja, H. H. Joshi, "structural properties of magnesium and co-substituted lithium

- ferrites" *Mater. Lett.*, Vol.57, Feb. 2003 pp. 4049-4053.
- [4] H. M. Widatallah, C. Johnson, F. Berry, M. Pekala, "Synthesis, structural, and magnetic characterisation of magnesium-doped lithium ferrite of composition  $\text{Li}_{1-x}\text{Fe}_{2.5x}\text{O}_4$ " *Solid state Commun.*, Vol. 120 Oct. 2001, pp. 171- 175.
- [5] G. M. Argentina, P. D. Baba, Microwave lithium ferrite: an overview, *IEEE Trans.*, Vol. 22, June 1974, pp.652-658.
- [6] S. Verma, P.A. Joy, "Magnetic properties of super paramagnetic lithium ferrite nanoparticles" *J. Appl. Phys.* Vol.98 Dec. 2005, pp. 124312 - 124312-9
- [7] Yen-PeiFu, "Microwave induced combustion synthesis of  $\text{Li}_{0.5}\text{Fe}_{2.5x}\text{Cr}_x\text{O}_4$  powder and their characterization", *Mater. Res. Bull.* Vol. 41, Oct.2005, pp. 809-816.
- [8] Yen-PeiFu, Shao-Hua Hu, "Electrical and magnetic properties of magnesium-substituted lithium ferrite", *Ceram. Int.* Vol.36, Jan. 2010, pp.1311-1317
- [9] D. Ravinder, "Elastic behaviour of lithium ferrites", *Mater. Lett.*, 45(2), March 2000, pp. 125-127.
- [10] S.Manjura Hoque, M. Samir Ullah, F.A. Khan, M.A. Hakim, D.K. Ssha, "Structural and Magnetic properties of Li-Cu mixed spinel ferrites" *Physica B* Vol. 9 Feb.2011, pp. 1799-1804.
- [11] Nutan Gupta, Mukesh C. Dimri, Subhas C. Kashyap, D.C. Dube, "Processing and properties of cobalt-substituted lithium ferrite in GHz frequency rang", *Ceram. Int.*, Vol. 30, April 2004, pp. 1623-1628.
- [12] J. Smith, and H.P.J. Wijn "Ferrites", Philips Technical Library, Eindhoven, The Netherlands (1959).
- [13] Hari Babu, Ph. D Thesis, "Study Of Microwave Lithium Ferrite Substituted With  $\text{Nb}^{5+}$  And  $\text{V}^{5+}$  Ions And Its Potential As A Memory Device" Submitted To Andhra University, India, June 1998.
- [14] S. S. Bathu, V. K. Lakhani, A.R. Tanna, N. H. Vasoya, J. U. Buch, P. U. Sarma, U. N. Trivedi, H. H. Joshi and K. B. Modi, "Effect of nickel substitution on structural, infrared and elastic properties of lithium ferrite" *Indian J. Pure Appl. Phys.*, Vol.45 April 2007, pp. 596-608.
- [15] A. D. P. Rao, Ph. D thesis, "structural, magnetic and electrical studies on Sn/Nb substituted Mn-Zn ferrites" Submitted to Andhra University, India, 1995.
- [16] M. Goodarz Naseri, E. Bin Saion, H. Abbastabar Ahangar, M. Hashim, A. H. Shaari, "Synthesis and characterization of manganese ferrite nanoparticles by thermal treatment method" *J. Magn. Mater.*, vol.323 Feb.2011, pp. 1745-1749.
- [17] A. B. Naik, S. R. Sawant, S. R. Sawant, S. A. Patil and J. I. Power, "On the variation of a.c. susceptibility with temperature for some Cu-Li ferrite", *Bull. Mater. Sci.*, Vol. 11(4) Dec.1988, pp. 315-318.
- [18] S. B. Murthy and T. S. Rao, *Phys. Stat. Sol.*, "Elastic behaviour of mixed Li-M ferrites", *Physica stat. solidi(a)*, Vol. 88, March 1985, pp. 239-243.
- [19] B. C. Cullity, "Elements of X-ray Diffraction" Addison-Wesely, Publishing Co. Inc (1959)
- [20] K. S. Lakshmi, B. Ramesh, A. D. P. Rao, P. M. RAO and S. B. Raju, "Effect of Sb/Mo on magnetic properties of Mn-Zn ferrites" *J. Mag. Soc. Japan*, Vol. 22, Supp. S1, 1998, pp. 37-40.
- [21] D. Vijayalakshmi, Ph. D thesis, "Structural, Magnetic and Mössbauer studies of antimony and molybdenum substituted Mg-Mn ferrites" Submitted to Andhra University, India, Nov.2003.
- [22] H. M. Widatallah, C. Johnson, F. J. Beery, A. M. Gismelseed, E. Jartych, J. F. Marco, F. S. Gard, M. Pekala, "Synthesis and cation distribution of copper-substituted spinel-related lithium ferrite", *J. Phys. Chem. Solids*, Vol. 67 April 2006, pp.1817-1822.
- [23] C. Oetro Arean, J. L. Rodriguez Balnco, J. M. Rubio Gonzalez and M. C. Trobajoa Fernandez" Structural characterization of polycrystalline gallium-substituted cobalt ferrites" *J. Mater. Lett.*, Vol.9, Feb.1990 pp. 229-230.
- [24] R. L. Dhiman, S. P. Taneja and V. R. Reddy "Structural and Mössbauer Spectral Studies of Nanosized Aluminum Doped Manganese Zinc Ferrites" *Adv. Cond. Matter. Phys.*, Vol.2008 Nov.2008, ID 839536, 7pages
- [25] K. B. Modi, J. D. Gajera, M. C. Chhanbar, K. G. Baldha, H. H. Joshi, "Structural properties of magnesium and aluminium co-substituted lithium ferrite" *Mater. Lett.*, Vol. 57, Feb.2003, pp. 4049-4053.
- [26] K. B. Modi, J. D. Gajera, M. P. Pandya, H. G. Vora and H. H. Joshi, "Far infrared spectral studies of magnesium and aluminium co-substituted lithium ferrites", *Indian. Acad. Sci.*, Vol.62(5). Jan.2004 pp. 1173-1180.