Structural and Dielectric Studies of Nickel Substituted Lithium Nano Ferrites by Low Temperature Combustion Method

G. Aravind[1], G. Koteshwari[2], Abdul Gafoor[3], D. Ravinder[4]

[1,2,3,4]*Dept of Physics, Osmania University, Hyderabad-500007, Telangana-India*

ABSTRACT

Nano crystalline spinel ferrites having compositional formula $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ (where x= 0.0 to 1.0 with step of 0.2) have been prepared by non conventional low temperature citrate gel auto combustion method. The synthesized ferrite powders were sintered at 500^{o}C for 4 hours. The single phase cubic structure of the prepared samples was confirmed by X-ray diffraction analysis. By increasing in the Ni doping in the Li-Ni ferrites, the variations in the structural parameters like lattice parameter, crystallite size and X-ray density etc, were observed. The dielectric parameters like dielctric constant, dielectric loss tangent (tanδ) and A.C.Conductivity of the prepared samples were measured by using Agilent E4980A precession LCR meter at room temperature in the frequency range 20-2MHz. The dielctric constant(ε'), dielectric loss tangent (tanδ) and A.C.Conductivity of the prepared samples shows a normal dielectrc behaviour of ferrites with frequency which indicates the dielectric dispersion is due to the hoping of electrons between the Fe^{+2} and Fe^{+3} ions.A qualitative explanation was given for composition and frequency dependent dielectrical properties of the prepared Li-Ni ferrite samples.

Keywords: Ferrites, Citrate gel method, X-ray diffraction and dielectric properties

1. INTRODUCTION

Ferrospinels have interesting structural, electrical and magnetic properties and widely used in many important applications such as microwave devices like circulators, phase shifters,memory cores, magnetic recording media,transformers, choke coils, high frequency instruments, data storage, noise filters and recording heads, owing to their high magnetic permeabilities and low magnetic losses [1,2]. The properties of spinel ferrites depend upon the method of preperation substitution of suitable cations, heat-treatment,annealing conditions and pH value etc.[3].

Ferrite materials are insulating iron oxides. Unlike most materials, they posses high permeability and moderate permitivity operating at different frequencies. Due to their small eddy current losses, there exist no other materials with such wide ranging value to the electronic applications in terms

of energy production and transmission and telecommunication applications. Present, nano ferrites has been the subject of many scientists all over the world because of novel properties exhibited by nanoparticles. The bulk material properties were vary drastically when their size approaches the nanoscale [4]. In ferrites, grain size reduction and grain boundary modifications results a high frequency properties such as resistivity and quality factors. Smaller grain size will provide large number of grain bounderies as barriers for the electron hoping between the different ions so as to increasing the resistivity and decreasing the eddy current losses in ferrites [5].

Lithium ferrites and substituted Lithium ferrites have become candidates of the most attractive materials for microwave applications especially as a replacement of garnets. Mixed lithium ferrites has low cost, square hysterisis loop, high Curie temperature which resuts superior high temperature perfomance are the other important properties that make them promising materials for microwave applications [6-8].

Nano crystalline ferrite materials synthesised by various preperation techniques incuding glass-ceramic method [9], hydrothermal method [10], solgel method [11], coprecipitation method [12], citrate gel method [13]. Many scientists have studied frequenccy dependence on the dielectric properties of Li-Co [14], Li-Mg [15], Li-Ge [16]. Among the various preperation methods citrate gel auto combustion method has attracted the attension of solid state chemist, physist and material scientist etc due to the fact that product powder samples with high purity and homogenity can be obtained. This is because the mixing of constituent cations takes place on an atomic scale in the precursor itself, therby lowering the temperature during formation of required ferrites. The novel properties were observed in this preperation method [17]. Present communication we report the structural properties of Li-Ni nano crystalline ferrites, and detailed investigation of the composition and frequency dependence of the dielectric properties of the Ni^{+2} substituted Lithium ferrites and the results studied.

2. EXPERIMENTAL

Ni substituted Lithium ferrites with compositional formula $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ (where x= 0.0 to 1.0 with step of 0.2) have been prepared low temperature citrate gel auto combustion method.

Starting Chemcals:

(i) Ferric nitrate ($Fe(NO_3)_2 9H_2O$)

(ii) Nickel nitrate ($Ni(NO_3)_2 6H_2O$)

(iii) Lithium nitrate ($LiNO_3$)

(iv) Citric acid ($C_6H_8O_7.H_2O$) and Ammonia solution (NH_3).

ISBN: 978-93-83083-88-6

The detailed preperation method of citrate gel auto combustion method was explained in our earlier publication [18].The synthesised powders were sintered at 500^{o}C for 4 hours in air at a slow heating rate of 5^{o}C/min and then furnace cooled. X-ray diffraction analysis of the prepared ferrite powders were performed by using Philips diffractometer with CuK_{α} radiation with wavelength 1.5405A^{o}. The average crystalline size of the ferrites was determined from the measured width of their diffraction pattern using the Debye scherrer's formula

$D=0.91\lambda/\beta\cos\theta$ (1)

Where λ is the wavelength of the X-ray used for diffraction,
β is the full width half maximum (FWHM) in radians.
θ is the diffraction angle.

The lattice constant was calculated using the follwing relation

$2d \sin\theta = n\lambda$ (2)

Where $d = \frac{a}{(h^2+k^2+l^2)^{1/2}}$ for fcc system.

Hoping length for tetrahedral site $d_A=0.25a\sqrt{3}$ A^{o} (3)

And for octahedral site $d_B=0.25a\sqrt{2}$ A^{o} (4)

For dielectric measurements powders were added with a small amount 2% PVA as a binder to press the powder into pellets of diameter of 13mm and thickness 2 mm by applying pressure of 5 tons. The final sintering temperature was again at 500^{0}C, afterwards the pellets were coated either side with silver paint for better electrical contact to measure thedielectricproperties.

Agilent E4980A Precision LCR meter was used for the dielectrical measurements of the prepared samples by using bellow formula [19]

The real part of dielectric constant (ε')= C_p / C_{air} (5)

Where C_p = Capacitance of the pellet in faraday
C_{air}= Capacitance of the air in faraday

The imaginary part of dielectric constant $\varepsilon'' = (\varepsilon')\tan\delta$ (6)

Where $\tan\delta$ is the dielectric loss tangent.
The A.C. conductivity was calculated using the following relation [20]
$\sigma_{ac} = 2\pi f \varepsilon_o(\varepsilon')\tan\delta$ (7)

Where ε_o = permitivity of free space = $8.85X10^{-12}$ F/m
Tan δ = dielectric loss tangent

3. RESULTS AND DISCUSSIONS

The X-ray diffraction pattern of the prepared Ni substituted Lithium nano ferrites were shown in fig (1). The X-ray diffraction pattern of the prepared samples were confirmed the well defined homogeneous single phase cubic spinel structure belonging to the space group Fd3m. Crystallite size of the prepared nano samples measured from the X-ray analysis was in the range 39-49nm.

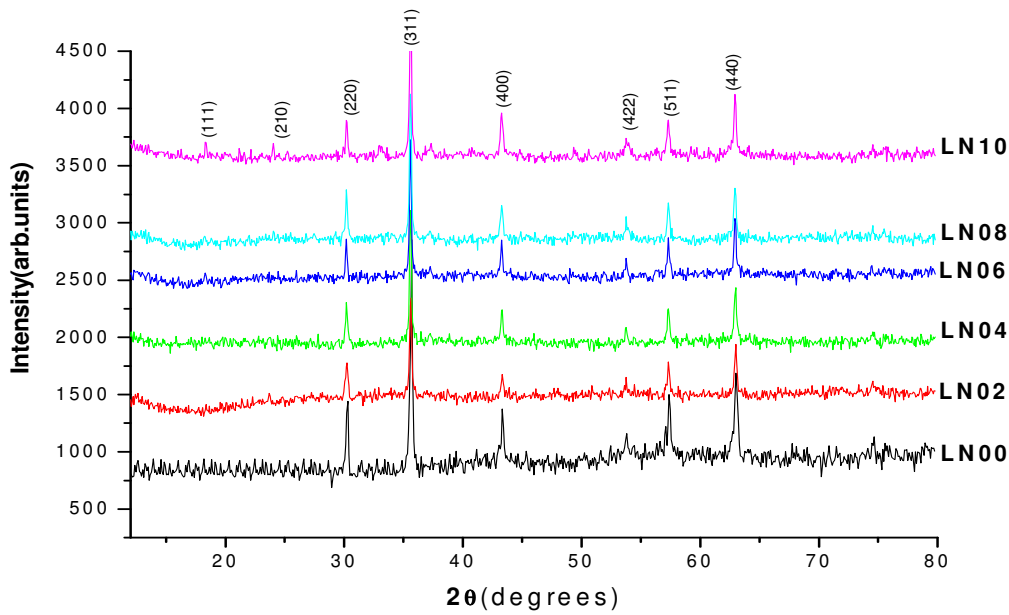
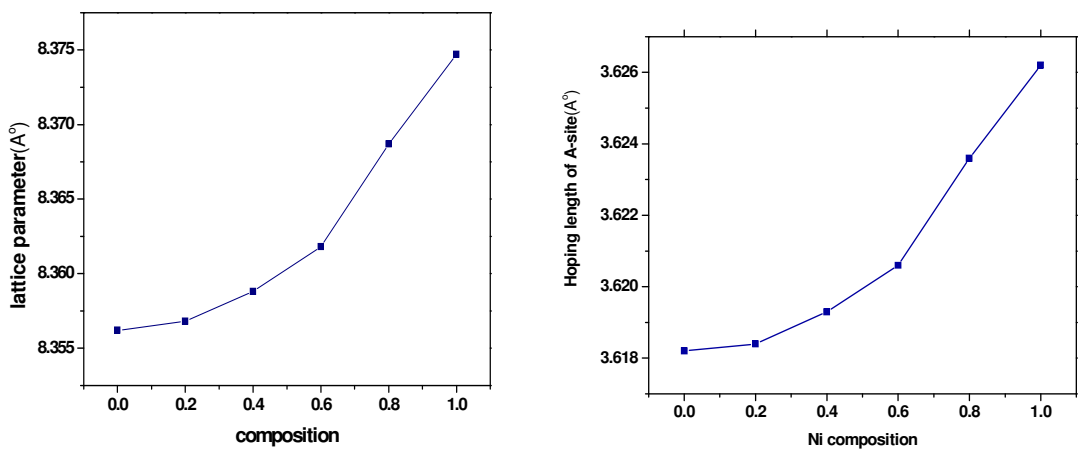


Fig (1) XRD pattern of the nano crystalline Li-Ni ferrites

Lattice parameter of the prepared samples was increased with increasing the Ni composition in the Li-Ni nano crystalline ferrites. This was expected because ionic radius of the Ni was (0.78A^o) greater than the ionic radius of the Li^{+1}(0.76A^o) and Fe^{+3}(0.67A^o) ions. Hoping length of A-site and B-site was observed to be increased with increasing with the Ni composition this is because hoping length of sites were proportional to the lattice parameters of the samples. The variation of lattice parameter (A^o) and hoping length of A-site increases with Ni composition which were shown in below fig (2a) & fig (2b) respectively.

Table1 Lattice parameter, Crystallite size Hoping length volume of the prepared Li-Ni samples

Ni content	Lattice Parameter (A^o)	Crystallite size(nm)	Hoping length for A-site(d_A) in A^o	Hoping length for B-site(d_A) in A^o	Volume of the Unit cell $(A^o)^3$
X=0.0	8.3562	41.90	3.6182	2.9539	583.480
X=0.2	8.3568	39.54	3.6184	2.9541	583.606
X=0.4	8.3588	45.35	3.6193	2.9548	584.025
X=0.6	8.3618	49.90	3.6206	2.9558	584.654
X=0.8	8.3687	41.30	3.6236	2.9583	586.103
X=1.0	8.3747	43.01	3.6262	2.9604	587.364



(a) **(b)**

Fig (2) Variation of lattice constant & hoping length of Li-Ni ferrites with composition

The dielectrical properties of the ferrites depends on the several factors including method of preperation, type and amount of substitution, sintering time and sintering temperature, particle size etc. The frequency dependence dielectrical properties of the prepared Li-Ni samples were shown in below Fig (3) to Fig (5).

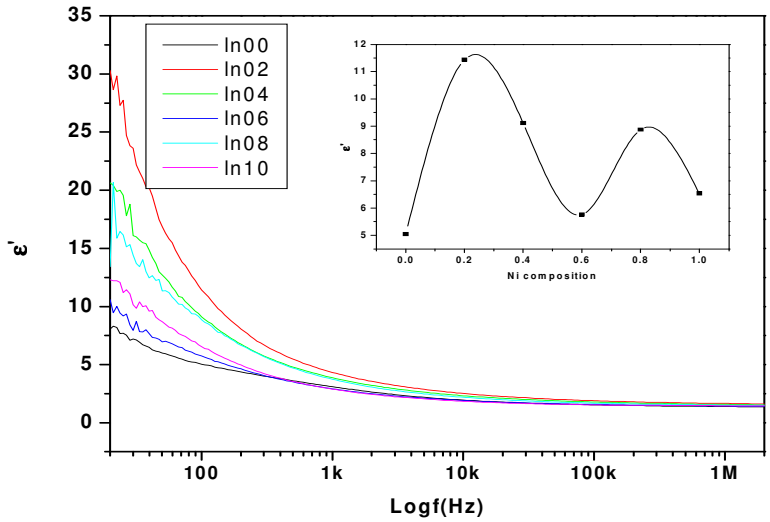


Fig (3). Variation of ε' with frequency and Ni Composition.

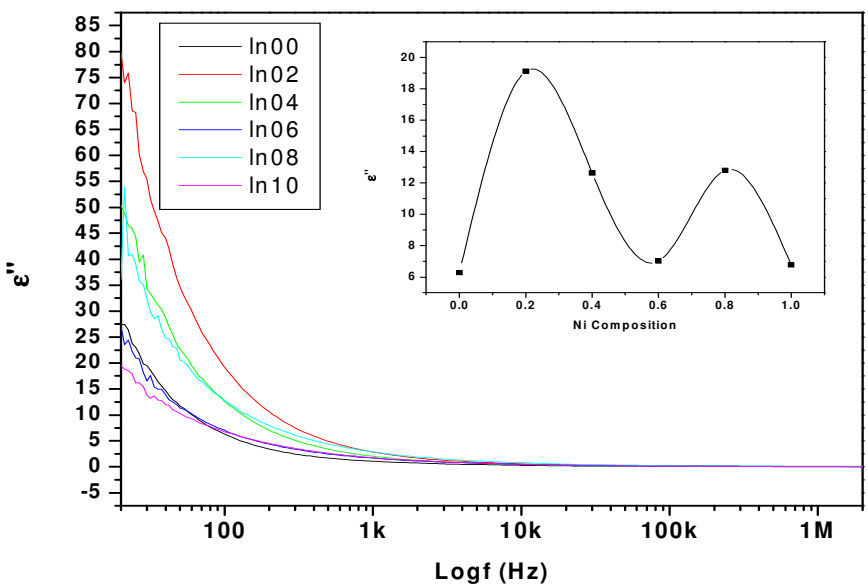


Fig (4). Variation of ε'' with frequency and Ni Composition.

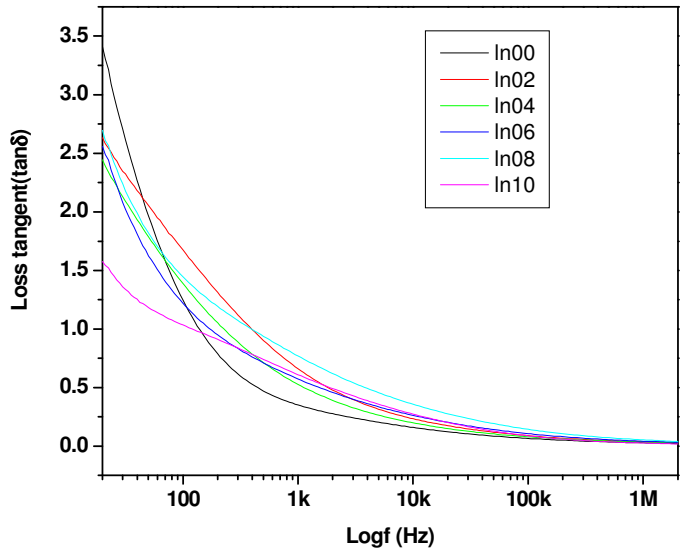


Fig (5). Variation of Loss Tangent with frequency of Li-Ni ferrites

From the above figures it is concluded that the value of the real part of dielectric constant (ε')and imaginary part of dielectric constant (ε'')at room temperature decreases continuously with increasing frequency after certain frequency the dielectric parameters does not change with frequency i.e. become independent of frequency. The explanation of behaviour of variation in the dielectric parameters in ferrites was similar to the coduction mechanism in ferrites [21]. The electron conduction mechanism can be explained by electron hoping between the same element having the different ionic states (Fe^{+3} and Fe^{+2}/ Ni^{+2} and $Ni^{+!}$) [22]. One can get the local displacements of electrons in the directions of the applied electric field, these produced displacements determine the polarisation in the ferrites. The main effect of induced polarisation is to decrease the field inside the ferrite material. Therefore the dielectric constant of the material may be decreased exponentially with increasing the frequency but at higher frequency hoping frequency of electrons does not follow frequency of applied electric field. Loss tangent of the material also decreases with frequency and these vlues are very less so these materials are sufficient for microwave applications.

The variation of dielectrical properties of Li-Ni nano ferrites with Ni composition was inserted seperately in Fig (3) and Fig (4) respectively. From these figures we conclude that room temperature dielectrical constants decreased with Ni concentration after an intial rise from Ni

equals to 0.0-0.2. It is seen that as Ni content is increased there is a decrease in the Fe^{+3} ions at the B-sites there by decreasing the hopping motion of electrons, which results the decreases the piling up of electrons at the grain boundary therefore the dielectric constant decreases. The same anomolous behaviour was also observed by some other researchers [23].

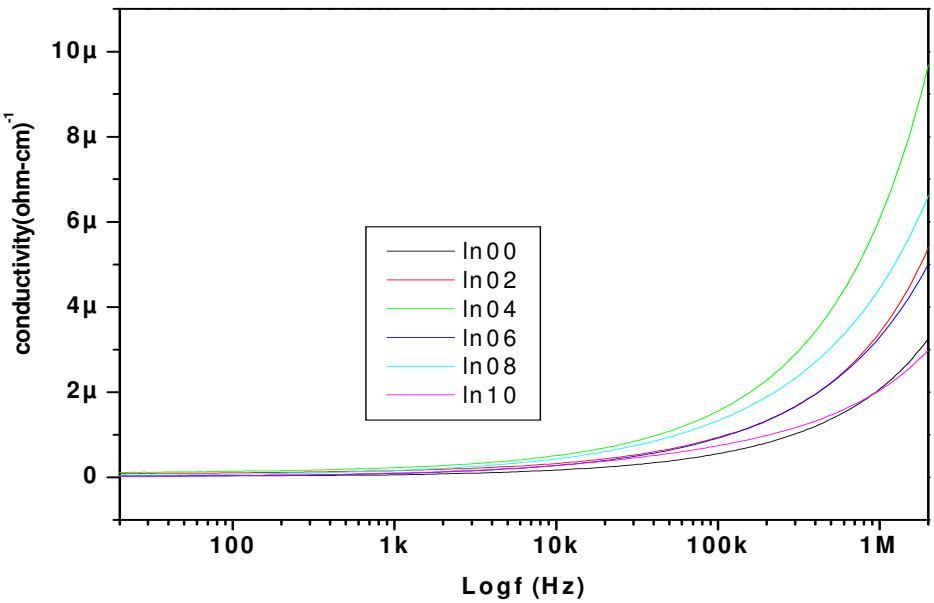


Fig (6) Variation of a.c.conductivity with frequency of Li-Ni ferrites

From the Fig (6) it was concluded that the a.c.conductivity of the prepared samples shows dispersion with respect to frequency. It increases slowly at lower frequencies, but after certain frequency it increases rapidly, this behavior can be explained by Koop's theorem [24], which supported that the ferrite compact act as amultilayer condensor. According to koop's model in ferrite, grain and grain boundaries have different properties. The process of multilayer condensor increases with frequency, which results the conductivity of ferrite samples increses.

4. CONCLUSIONS

Ni^{+2} ions when substituted in the basic lithium ferrite effect its structural and dielectrical properties. The crystallite size of the prepared samples was in the range of 39-49nm which reveals the nano crystalline structure.By increasing the Ni concentration increse the lattice parameter and hoping

length of A-site and B-site. The dielectric constant and dielectric loss tangent were observed to be decrease with the increase in frequency, which was the common nature of any semiconducting ferrites. The ac conductivity of the prepared samples were observed to be increased with increasing the frequency.

5. ACKNOWLEDGEMENT

The authors are very grateful to Prof.K.Venu Gopal Reddy, Head, Department of Physics, University College of Science,OsmaniaUniversity,Hyderabad. The authors are very thankful to UGC, New Delhi, for their financial assistance through Major research Project (M.R.P).

REFERENCES

[1] G.Blasse,Philips Res.Rep.(Netherlands) 20 (1965) 528.
[2] J.B.Goodenough, Magnetism and Chemical bond, Wiley, New York, 1956
[3] C.Liu,Z.Lan,X.Jiang,Z.Yu,K,Sun,L.Li,P.Liu, J Magn.Magn.Mater 320 (2008) 1335.
[4] A.M.Kumara,M.C.Vermaa,C.L.Dubeb,K.H.Rao,S.C.Kashyap, , J Magn.Magn.Mater 320(2008) 1995-2000.
[5] Y.J.Yang, C.I.Sheu.S.Y.Cheng, H.Y.chang, , J Magn.Magn.Mater 284 (2004) 220-228.
[6] S.A.Jadhav, , J Magn.Magn.Mater 224 (2001) 167-172.
[7] A.M.Shaik,C.M.Kanamadi,b.K.Chogale, Material Chemistry and Physics 93 (2005) 548-551.
[8] S.A.Jadhav, Material Chemistry and Physics, 65 (2000) 120-123.
[9] Ahmed M.El-Sayed, Esmat M.A.Hamzawy, Monatshefte fur Chemie 137 (2006) 1119.
[10] Chaoquan Hu, Zhenghong Gao, Xiaorui Yang, J Magn.Magn.Mater 320 (2008) L70.
[11] Khalid Mujasam Batoo, Shalendra Kumar, Chan gyu Lee, Alimuddin, Curr Appl Phys,9 (2009) 1072.
[12] I.Soibum,S.phanjoubam,C.Prakash, J Magn.Magn.Mater 321 (2009)2779.
[13] Nutan Gupta, S.C.Kashyap,D.C.Dube,Phy,sat sol,204, no.7, 2441-2452 (2007)/ DOI10.1002/pssa.200622146
[14] Y.C.Venudhar, k.Satya Mohan,Mater Lett.54 (2002) 135
[15] S.S.Bellad,B.K.Chougale,Mater Chem Physics,66 (2000) 58.
[16] D.Ravinder, A.Chandrashekhareddy,Mater letters 57 (2003) 2855.
[17] Amarendra K.Singh,T.C.Goel, T.G.Goel,R.G.Mendiratta,O.P.Thakur, chandra Prakash, j Appl.Phy.91 (2002) 6626.
[18] G.Aravind, D. Ravinder, Int J of Engg reseach Applications Vol3, Issue6, nov- Dec 2013, pp1033-1039.
[19] Dr.S.L.Gupta,Sanjeev gupta," Electricity, Magnetism and Electronics". First edition Jai prakash nath and company.
[20] Erum Pervaiz, I.H.Guil J Magn.Magn.Mater 324 (2012) 3695-3703.
[21] K.Iwauchi, J of Applied Physics, 10 (1971) 1520.
[22] G.H.Jonker, J Phys Chem Solids,9 (1959) 105.

[23] Ibetombi Soibam,Sumitra Phanjouban,H.B.Sharma,H.N.K.Sharma, Solid State Communications 148 (2008) 399-402.

[24] C.G.Koops, Phys Rev.83 (1951) 121.

CAPTIONS TO THE FIGURES

Fig (1) XRD pattern of the nano crystalline Li-Ni ferrites

Fig (2) Variation of lattice constant & hoping length of Li-Ni ferrites with composition

Fig (3) Variation of ε' with frequency and Ni Composition

Fig (4) Variation of ε'' with frequency and Ni Composition

Fig (5) Variation of Loss Tangent with frequency of Li-Ni ferrites

Fig (6) Variation of a.c.conductivity with frequency of Li-Ni ferrites

CAPTIONS TO THE TABLES

Table1 Lattice parameter, Crystallite size Hoping length volume of the prepared Li-Ni samples