

Thermo-Analytical and SEM Studies on Li^{1+} Substituted Ni-Zn Ferrites

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Abstract: Ni-Zn Ferrites systems exhibit remarkable magnetic properties and finds applications in devices such as inductor cores, magnetic heads converters electromagnetic wave absorbers etc. coupled with low production cost. The soft chemistry approaches make it possible to synthesize homogenous dense and smaller particle size ferrites at relatively low temperatures. Lithium oxalate solution was synthesized by adding hot solution of oxalic acid with lithium carbonate¹, was filtered and cooled, when lithium oxalate was precipitated and then dried. Ni-Zn-Fe oxalate complexes were synthesized by co-precipitation technique using oxalate precursor². Lithium oxalate was mixed to the solid solution of Ni-Zn-Fe oxalate complex for 2 to 3 hours. Thus solid solution of oxalate complex having general composition $\text{Ni}_{0.32}\text{Zn}_{0.68-2x}\text{Li}_x\text{Fe}_{2+x}(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ with $x=0.00, 0.025, 0.05, 0.075, 0.10, 0.15$ & 0.20 was obtained by method suggested by Wickham³.

STA studies were carried out on above synthesized oxalate complex in order to determine the ferritization temperature. The temperature at which ferrite phase is formed and to fix the number of water molecules in oxalate complex for proposing the formulae of oxalate complex. The oxalate complexes were decomposed at their respective ferritization temperatures as revealed from thermograms (TG). STA studies revealed formation of single spinel phase ferrites in the temperature range $196 - 370^\circ\text{C}$. Li^{1+} plays a significant role in lowering of ferritization temperature. Increasing Li^{1+} contents leads to the lowering of ferritization temperature. This has been attributed to earlier initiation of decomposition of Li^{1+} in the oxalate complex.

Characterization of samples was done by XRD techniques. XRD's of oxalate complex decomposed at 350°C for 3 hours and sintered at

1050°C for 24 hours were recorded. XRD's showed formation of a single spinel phase at lower temperature. Lattice parameter showed a decreasing trend with increasing Li^{1+} content. This has been attributed to ionic sizes of cations involved. Tetrahedral bond length, tetrahedral radii, tetrahedral edge, unshared octahedral edge decrease with increase in Li^{1+} content. Octahedral bond length, octahedral site radii, shared octahedral edge increase with increase in Li^{1+} content.

Density measurement on sintered samples sintered at 1050°C for 24 hours were carried and by using xylene medium exhibit close resemblance. All compositions showed density values which are 97% of the theoretical values. Thus high density ferrites are obtained at low temperature lying in the range of 196 -370°C. High density plays a crucial role in enhancement of magnetic properties, such as, initial permeability, saturation magnetization, Coercive force. The increase in Li^{1+} content leads to lowering of density values.

SEM studies were carried out on sintered samples sintered at 1050°C for 24 hours in order to measure the grain size. SEM studies revealed formation of fully developed, close and compact grain structure. The grain size of Li^{1+} Ni-Zn ferrite is larger than that of Ni-Zn ferrites. This suggests Li^{1+} favors grain growth.

1. Introduction

The conventional ceramic technique^{1,2} for the synthesis of ferrite material places limitations such as requirement of high sintering temperature with long time, which may cause the evaporation of the elements such as Zn, Li etc., leading to formation of chemically inhomogeneous material^{3,4} with large particle size and low density⁵. Soft chemistry route overcome these limitations and thereby make it possible to synthesize homogeneous ferrite material with high density and smaller particle size^{4,6}. The oxalate precursor method is more convenient, since it yields a homogeneous product in short time. Schroder⁷ concluded that the decomposition of mixed oxalate is apparently a low temperature phenomenon. Moye et al⁸ have synthesized Ni-Zn ferrites from oxalate and oxalato hydrazinate precursor by decomposing them in air and controlled atmosphere. They have concluded that $\gamma\text{-Fe}_2\text{O}_3$ ferrite phase is achieved at 350 °C, which is easier to sinter and thereby lead to formation of a better magnetic material. V. K. Shankanarayan et al⁹ have prepared the ultra fine particle of Li ferrite at unusually low temperature of 240°C and 455°C by citrate precursors. The probable evaporation of Li during high temperature sintering in ceramic method led to synthesize the present Li doped Ni-Zn ferrite system by soft chemistry approaches. The present work report thermo-analytical and

Scanning Electron Microscopic (SEM) studies on Li^{1+} substituted Ni-Zn ferrites synthesized by oxalate precursor.

2. Experimental

The oxalates were synthesized by the method suggested by Wickham¹⁰ and later on modified by M. Bremer et al¹¹ for Mn-Zn ferrites. Lithium oxalate was synthesized by adding hot solution of oxalic acid with Lithium carbonate, was filtered and cooled, when Lithium oxalate was precipitated and then dried¹². Ni-Zn-Fe oxalate complex was synthesized by co-precipitation technique using oxalate precursor¹³. Lithium oxalate was mixed to the solid solution of Ni-Zn-Fe for 2-3 hrs. Thus the solid solution of co-precipitated oxalate complexes having general composition, $\text{Ni}_{0.32}\text{Zn}_{0.68-2x}\text{Li}_x\text{Fe}_{2+x}(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ was obtained. The oxalate complexes were decomposed at 350°C for 3 hours and sintered at 1050°C for 20 hours.

3. Results and Discussion

STA: Simultaneous Thermal Analysis

The representative STA (TG, DTG, DTA) of oxalate complex ($x = 0.025, 0.075$) have been given in Fig.1(a).and ($x=0.15, 0.20$) in Fig.1(b).

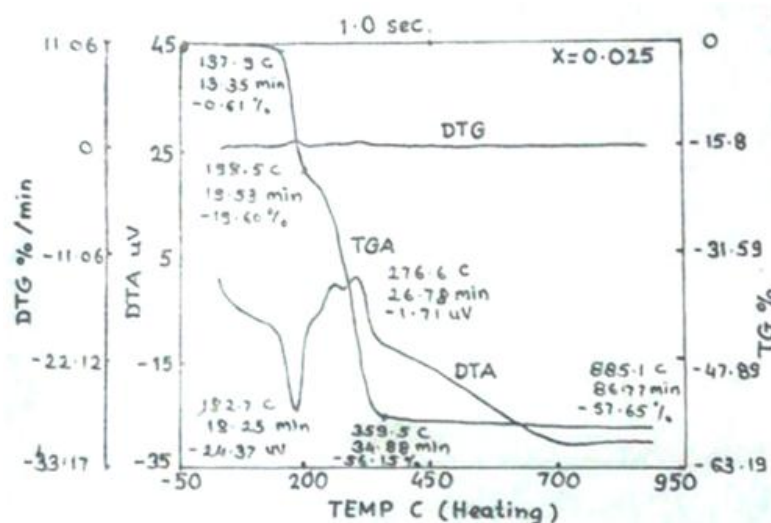


Fig. 1 (a)

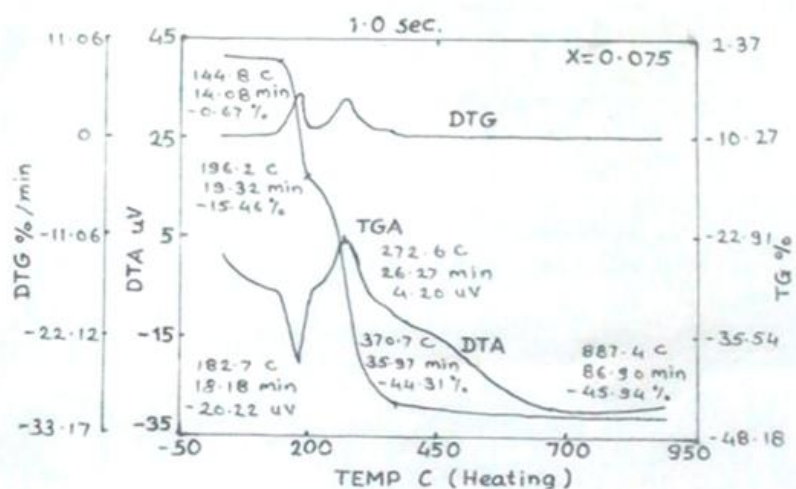


Fig. 1 STA charts for $\text{Ni}_{0.32}\text{Zn}_{0.68}-2x\text{Li}_x\text{Fe}_{2+x}(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ oxalate complexes.

Fig. 1(b)

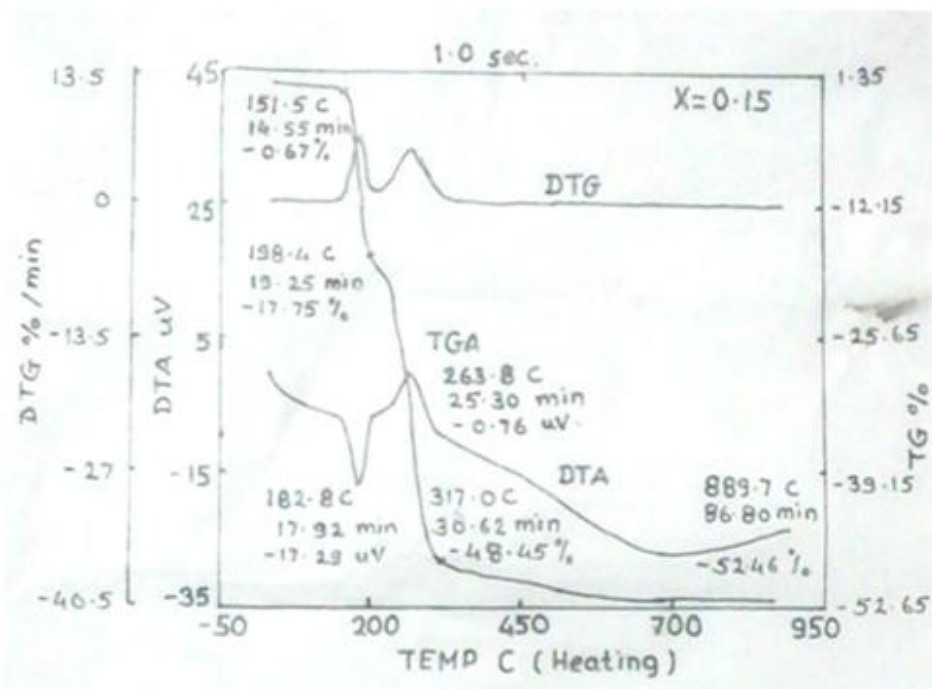


Fig. 2(a)

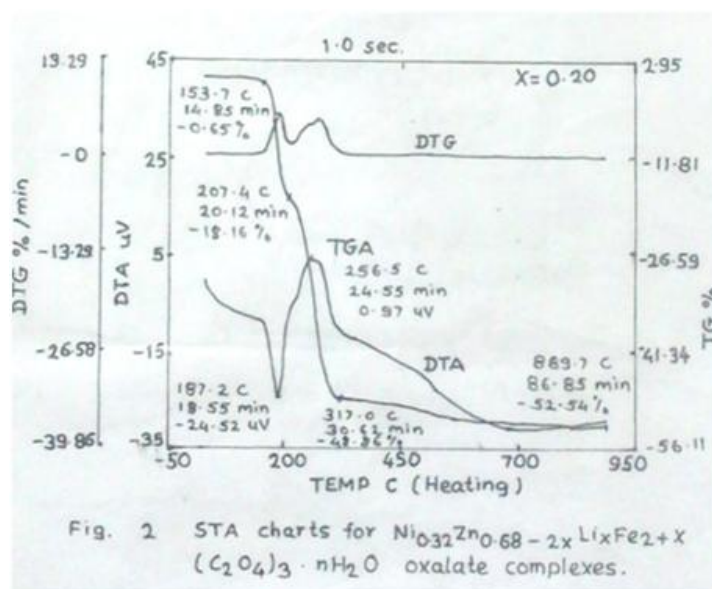


Fig. 2(b)

From STA charts, It is seen that thermal decomposition of present oxalate complexes occurs in two steps. Step I includes dehydration of oxalate complex (endothermic reaction – sharp peak). Step II indicates decomposition of dehydrated oxalate complex to requisite ferrite composition (exothermic reaction – less sharp peak). Dehydration and decomposition are single step process which indicate the formation of homogeneous phase during synthesis and get completed in the temperature range 196°C to 207°C and 317°C to 370°C respectively.

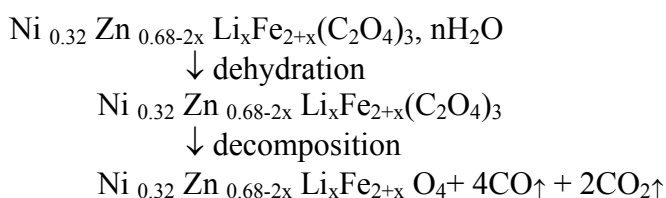
Table 1: Data on onset and termination temperature and time in min. during dehydration and decomposition obtained from TG for $\text{Ni}_{0.32}\text{Zn}_{0.68-2x}\text{Li}_x\text{Fe}_{2+x}(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$

X	Dehydration in $^\circ\text{C}$				Decomposition in $^\circ\text{C}$		
	Onset temp.	Time (min.)	Termination temp.	Time (min.)	Onset temp.	Termination temp.	Time (min.)
0.00	159.5	15.33	213.3	20.50	213.3	352.7	33.67
0.025	137.9	13.35	198.5	19.53	198.5	359.5	34.88
0.075	144.8	14.08	196.2	19.82	196.2	370.5	35.97
0.15	151.5	14.55	198.4	19.25	198.4	317.0	30.62
0.20	153.7	14.85	207.4	20.12	207.4	317.0	30.62

Table 1 includes onset and termination temperature and time taken in min. during dehydration and decomposition process from TG. It is observed that for lower content of Li^{1+} , termination temperature is around $360\text{--}370^\circ\text{C}$

and for higher content, it is around 317°C, which is quite lower than the temperature mentioned above. This may be due to earlier initiation of decomposition of Li^{1+} in oxalate complex. The ferritization and decomposition processes occur simultaneously as nascent metal oxides are highly reactive. Hence ferritization temperature (the temperature at which ferrite phase is formed) get lowered. After completion of second stage, TG curve is nearly a straight line running almost parallel to temperature axis, which indicates the absence of any further change i.e simultaneous occurrence of completion of decomposition and ferrite formation in TG behavior and thereby stability of resultant ferrite. According to Dollimore et al¹⁴ the decomposition of oxalate complex MC_2O_4 (where $\text{M}=\text{Zn}, \text{Mg}, \text{Cu}$ etc.) produce oxide as an end product, $\text{MC}_2\text{O}_4 \rightarrow \text{MO} + \text{CO}\uparrow + \text{CO}_2\uparrow$

In view of the scheme given by Dollimore et al¹⁴ the decomposition scheme for present solid solution of oxalate complex can be generalized as,



DTG peaks are clear for oxalate complex with $x=0.075, 0.15, 0.20$. DTA peaks are sharp corresponding to dehydration and decomposition process. DTA peaks alike TG run almost parallel to the temperature axis, which support the simultaneous occurrence of decomposition of oxalate complex and ferritization (ferrite phase formation). There is close agreement between the onset temperature and termination temperature during dehydration and decomposition process is revealed from TGA and DTA.

XRD: X-ray Diffraction

The representative X-ray patterns of decomposed and sintered powder ($x = 0.075$) have been given in Fig.3. It is observed that all allowed planes for spinel ferrites are formed at 350°C and no new planes appear after sintering at 1050°C, which indicates the formation of single spinel phase. With increasing temperature, peak intensity grows due to crystallinity increase at simultaneous decrease of half intensity width. Data on bond length, site radii, tetragonal edge, shared and unshared octahedral edges have been calculated from the relations

$$d_{AX} = a_0 \sqrt{3} (u-1/4)$$

$$d_{\text{BX}} = a_0 (3u^2 - 11/4 u + 43/64)^{1/2}$$

$$d_{\text{XX}} = a_0 \sqrt{2} (2u - 1/2)$$

$$d'_{\text{XX}} = a_0 \sqrt{2} (1 - 2u)$$

$$d''_{\text{XX}} = a_0 (4u^2 - 3u + 11/16)^{1/2}$$

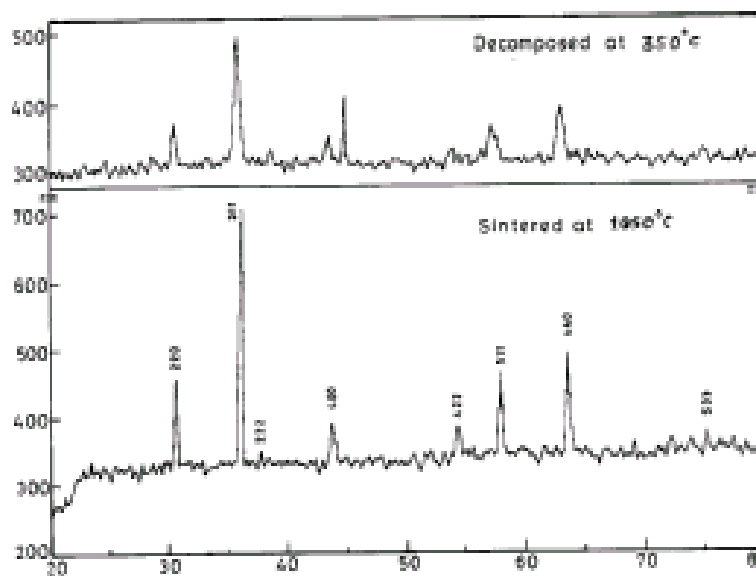


Fig. 3 XRD pattern for $\text{Ni}_{0.32}\text{Zn}_{0.68-2X}\text{Li}_X\text{Fe}_{2+X}\text{O}_4$ ($X = 0.075$)

From Table 2, it is seen that lattice parameter decreases with increase in Li^{1+} content which may be attributed to ionic sizes of cations involved i.e. Li^{1+} ions are replaced larger Zn^{2+} ions. It is also observed that with addition of Li^{1+} , tetrahedral bond length, tetrahedral site radii, tetrahedral edge, unshared octahedral edges decreases whereas octahedral bond length, site radii and shared octahedral edge increases.

Table 2. Data on onset, peak and termination temperature during dehydration and decomposition obtained from DTA for $\text{Ni}_{0.32}\text{Zn}_{0.68-2X}\text{Li}_X\text{Fe}_{2+X}(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$

X	Dehydration in $^{\circ}\text{C}$			Decomposition in $^{\circ}\text{C}$		
	Onset temp.	Peak temp	Termination temp.	Onset temp.	Peak temp	Termination temp.
0.00	159.5	188.1	213.3	213.3	252.5	352.7
0.025	137.9	182.7	198.5	198.5	276.6	359.5
0.075	144.8	182.7	196.2	196.2	272.8	370.5
0.15	151.5	182.8	198.4	198.4	263.8	317.0
0.20	153.7	187.2	207.4	207.4	256.5	317.0

Table 3. Data on lattice parameter (a), Bond length (d_{AX}, d_{BX}), site radii (r_A, r_B), tetrahedral edge (d_{XX}), shared and unshared octahedral edge (d'_{XX}, d''_{XX}) for $Ni_{0.32}Zn_{0.68-2x}Li_xFe_{2+x}O_4$ ferrite system.

X	a	d_{AX}	d_{BX}	r_A	r_B	d_{XX}	d'_{XX}	d''_{XX}
0.00	8.385	194.20	202.46	56.20	64.46	317.14	275.78	296.81
0.025	8.383	193.53	202.74	55.53	64.74	316.04	276.68	296.60
0.050	8.382	193.22	202.72	55.22	64.72	315.53	277.12	296.57
0.075	8.380	192.74	203.02	54.74	65.02	314.75	277.77	296.50
0.10	8.377	192.38	203.12	54.38	65.12	314.16	278.15	296.40
0.125	8.374	191.74	203.40	53.74	65.40	313.12	279.01	296.30
0.15	8.371	191.39	203.34	53.39	65.34	312.54	279.39	296.09
0.175	8.369	190.89	203.61	52.89	65.31	311.73	280.01	295.99
0.20	8.365	190.51	203.70	52.51	65.70	311.12	280.36	295.86

SEM: Scanning Electron Microscopy

The SEM photograph for composition with $x=0.075$ shown in Fig.3.

Table 4. Data on average grain size (Dav.) for $Ni_{0.32}Zn_{0.68-2x}Li_xFe_{2+x}O_4$ ferrite system.

X	Average grain size in um		
	Dmin.	Dmax.	Dav
0.00	0.33	1.6	0.73
0.025	0.39	2.45	1.82
0.075	0.32	2.52	1.76
0.15	0.34	2.19	1.52
0.20	0.51	2.84	1.94

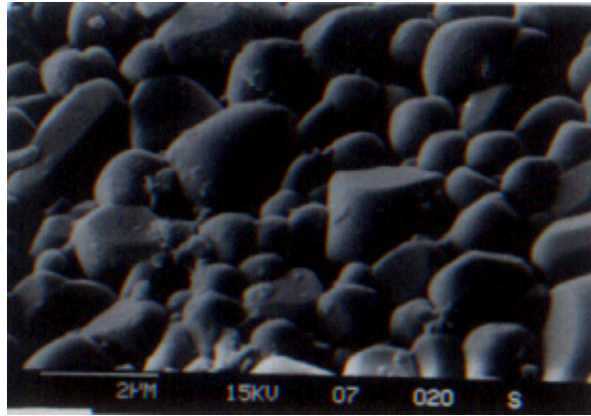


Fig. 4 SEM photograph for $Ni_{0.32}Zn_{0.68-2X}Li_xFe_{2+x}O_4$ ($X=0.075$)

From Fig.4 average grain size has been calculated and reported in Table 3. Grain size has been calculated as follows-

1. Drawing a diagonal on the photograph
2. Measuring the maximum unidirectional particle size in vertical direction against the diagonal
3. Averaging the maximum unidirectional particle size.

The following observations have been made –

1. Most of grains are fully developed. However there also appear some grains with round shape indicating that the grain growth is not complete.
2. Grains are very close but for some position where there are pores.
3. The grain size of Li^{1+} substituted Ni-Zn ferrite composition is larger than that of Ni-Zn ferrite composition, suggesting that Li^{1+} favors the grain growth although there is no predictable grain size variation.
4. There is clear distribution of grain size.

Density Measurement

Table 5.Data on Density obtained from X-ray, using xylene medium and from mass/volume for $\text{Ni}_{0.32}\text{Zn}_{0.68-2x}\text{Li}_x\text{Fe}_{2+x}\text{O}_4$ ferrite system

X	Density obtained from		
	X-ray	Xylene	Mass/volume
0.00	5.384	5.03	4.50
0.025	5.349	5.20	3.94
0.050	5.313	5.22	4.29
0.075	5.278	5.20	3.95
0.10	5.245	5.11	3.80
0.125	5.212	5.09	3.59
0.15	5.178	5.02	3.68
0.175	5.145	5.03	3.71
0.20	5.113	5.00	3.28

Table 4 summarizes, the values of density obtained from X ray , from physical dimensions and using xylene medium.

The X-ray density is determined from the formula

$$D_x = 8M/Na^3,$$

where M is molecular weight of the composition, N is the avagodrous number and a is the lattice parameter,

Density from xylene medium is determined from the relation

$$D = w\rho / w - w',$$

where w is sample weight in air, w' is sample weight in xylene and ρ is density of xylene.

Density from the physical dimension is determined by $d = \text{Mass} / \text{volume}$

The following observations have been made –

1. Densities obtained pyknometrically using xylene medium and those obtained from X-ray are comparable. Densities obtained from
2. With addition of Li^{1+} , the density values shows decreasing trend, since density of Li ferrite is 4.75 gm/cm^3 .
3. All the composition exhibits large density $>97\%$. Increased reactivity of fine powder is responsible for achieving density values almost near to X-ray density.

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