



Microstructure and Infrared Absorption Spectroscopic Study of Zn Substituted Li-Cu Ferrites.

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Abstract

In view of wide ranging applications mixed Lithium Zinc ferrites have been chosen for the present study. An attempt has been made in the present communication to report the structural properties of Zn substituted Li-Cu ferrite synthesized using microwave induced combustion synthesis route. The ferrites of the composition Li $_x$ Zn $_{(0.6-2x)}$ Cu $_{0.4}$ Fe $_2O_4$ (X=0.05, 0.1, 0.15, 0.2, 0.25, 0.3) at different chemical reaction temperature (100 °C, 125 °C and 150 °C) were prepared using non-conventional microwave sintering method. The structural properties and IR absorption spectra were investigated. Lattice parameter, crystalline size, grain size and absorption bands shows variation with Zn concentration. Far infrared absorption spectra show four absorption bands. The grain size is determined using SEM. The average value of the grain size for all the samples is found to be in the 64 nm to 98nm. The force constants have obtained from the infrared absorption band and their dependence with the internuclear distance has been discussed. The advantage of this method is its lower sintering temperature and time compared to the conventional ceramic technique and direct formation of nano-ferrites without ball-milling.

Keywords: Microwave sintering, X-ray diffraction, IR absorption spectra, grain

Introduction

Lithium ferrites and lithium based ferrites have become important materials for microwave application especially as a replacement for garnets owing to their low cost, Squareness of the hysteresis loop along with superior temperature performance due to a high Curie temperature and other prominent properties that have made them very promising candidates for microwave devices. Several studies have been reported with the addition of divalent, trivalent and tetravalent ions in lithium ferrite¹⁻³.

The infrared spectroscopic technique is based upon the fact that a chemical substance shows marked selective absorption in the infrared region. Various bands present in IR spectrum correspond to the characteristic functional groups and bonds present in the chemical substance. Hence, an IR spectrum of a chemical substance is the finger print for its identification ⁴⁻¹⁰. The IR spectroscopy is used to





determine the local symmetry in crystalline and nanocrystalline solids and also to study the ordering phenomenon in ferrites. Therefore in the present communication, we report on the microstructure, effect of grain boundary and infrared studies of this ferrite.

Materials and Methods

Zinc substituted Lithium copper ferrite having general formula of Li $_x$ Zn $_{(0.6-2x)}$ Cu_{0.4}Fe₂O₄ (X=0.05, 0.1, 0.15, 0.2, 0.25, 0.3) have been prepared at three different chemical reaction temperature using non-conventional microwave sintering method. Ferric nitrate, Zinc nitrate, Copper nitrates, Lithium nitrate-AR grade were used as the starting material. The stoichiometric proportions of the nitrates were weighed and added in 100 ml of distilled water to produce an aqueous solution. The solution kept in paraffin oil bath at three different chemical reaction temperature 100°C, 125°C and 150°C with constant stirring using the magnetic stirrer for three hours, in which the release of nitrates fumes results into the formation of thick slurry. The slurry was then transformed into the modified microwave oven (Model-GMS 17M07 WHGX). The microwave assisted combustion synthesis involving hydrothermal reactions were carried out in modified domestic microwave oven operating at maximum power output of 700 W. The irradiation was given in the form of pulses for nearly 30 to 32 minutes and the process was stopped when nitrous gases were evaporated completely. Finally the required brown coloured composition is formed. The obtained ferrite powder was then crushed in agate morter.

Crystal structure was determined from XRD data. The completion of the solid state reaction was confirmed by x-ray diffraction pattern taken on powder samples using a D8 Advance by M/s Bruker Axs, GMbH, Germany. X-ray diffractometer. The IR spectra were recorded on a FTIR instrument GJC IASCO (CHEM) (Model name FTIR 4100 Type A, serial number – C193161016) for all samples in KBr medium in the range 450 to 800 cm⁻¹.

The scanning electron micrographs were taken using SEM instrument JSM-7600 F (Magnification X 25 to 1,000,000)

Result and Discussion

FTIR Study

Ferrites possess the structure of mineral spinel that crystallizes in the cubic form with space group $Fd_{3m} - o_h^{7}$ ^[7] it is generally known that the spinel ferrites exhibit four IR active bands, designated as v_1 , v_2 , v_3 and v_4 . The occurrence of these four bands has been rationalized on the basis of group, theoretical calculations employing space group and point symmetries, both in normal and inverse spinels.

The room temperature (300 K) infrared spectra for Li $_x$ Zn $_{(0.6-2x)}$ Cu $_{0.4}$ Fe $_2O_4$ (X=0.05, 0.1, 0.15, 0.2, 0.25, 0.3) are shown in fig. 1, 2, 3. It is noticeable that the main absorption bands v_1 and v_2 have appeared in all series of the investigated ferrite system. These two bands are common in almost all spinel ferrites. They are located around 600 cm⁻¹ and 400 cm⁻¹ respectively. In the present work the high



frequency band v_1 and the second absorption band v_2 are found in the range 570-600 cm⁻¹ and 450 to 498 cm⁻¹ respectively. These are attributed to tetrahedral and octahedral site complexes in spinel structure. The absorption bands obtained in the present communication are found to be in the range reported by many authors for lithium ferrite¹¹⁻¹³.

The values of v_1 are higher than those of v_2 indicating that normal modes of vibration of the tetrahedral complexes are higher than that of the corresponding octahedral site. This may be due to the shorter bond length of the tetrahedral site (1.89 A^0) than that of the octahedral site ¹⁴. The shift in band position is observed as a function of Zn concentration. This can be interpreted by the more covalent bonding of Fe^{3+} ions at the A-sites than B sites.

The centre frequency of the bands v_1 and v_2 show a slight variation for the sample prepared at 100 °C. It is known that increase in site radius reduces the fundamental frequency and therefore the centre frequency should shift towards lower frequency side. Samples prepare at 100 °C shows the shift in absorption band. This result is corroborated by the A.c. susceptibility and magnetization measurement¹⁵ which have provided evidence of cluster formation in the samples. It is believed that the clusters cause local lattice distortion of the grain boundaries and act as charge traps of various depths. The process of trap recharging affects the absorption bands in IR spectra.

Sample prepared at reaction temp 125 °C and 150°C shows shifting gradually towards the lower frequency with increase in Zn content. From the x-ray diffraction study it is revealed that the lattice parameter and bond lengths R_A and R_B increase linearly with the increase with Zn content. It is well known that increase bond length reduces the fundamental vibrational frequency. Therefore the centre frequency of the bands v_1 and v_2 shifts towards the lower frequency side with the addition of Zn. The variation in v_1 and v_2 indicates that the method of preparation, the grain size and sintering temperature can influence the band positions ¹⁶.

The shift absorption bands with respect to the temperature of chemical reaction. This can be attributed to chemical kinematics. Chemical reaction temperature increases reaction rates because of the disproportionately large increase in the number of high energy collision causes formation of different product. Collisions only result in a reaction if the particles collide with enough energy to get the reaction started. This minimum energy required is called the activation energy for the reaction 1^{17} .

Another very small absorption bands around 665 cm⁻¹ and 546 cm⁻¹ have appeared in the IR spectrum of the samples for tetrahedral site. These bands are denoted by v_3 , v_4 . Such shoulders have been recorded also for the IR spectrum of Li_{0.5}Fe_{2.5}O₄ by many authors^{18, 19, 20}. It has been shown by Potakova et al. ²¹ that the presence of Fe^{2+} ions in ferrites can produce splitting or shoulders on absorption bands. This is attributed to the Jahn-Teller distortion produced by the Fe² ions, which cause local deformations in the lattice owing to the splitting of absorption bands.



According to Tarte ²², the high frequency band v_5 in the range 500 cm⁻¹ could be assigned to Li₁-O₂ complexes on the octahedral site. The absorption band v_6 around 520 – 540 cm⁻¹ has been observed only in samples of x = 0.05 synthesized at 150 °C. This band may be due to divalent metal ion-oxygen complexes in octahedral sites. Hence, its appearance can be considered as an evidence of the existence of the divalent iron ions Fe²⁺ ^[23]. As no such bands appears in samples for the remaining samples means there is no existence of divalent Fe²⁺ ions in octahedral sites.

The force constant Kt and Ko varies with the corresponding bond length. It is observed that Kt and Ko increase with increase in bond length. This behavior is attributed to the fact that oxygen can form stronger bonds with the metal ions even at larger internuclear separation²³.

Morphologies of sample

Magnetic and electrical properties sensitively depend on the microstructure of ferrite. Grain growth is closely related to the grain boundary mobility. Recrystallization and grain growth involve the movement of grain boundaries. The grain growth being a result of interparticle mass transport appears to the dominated by the bimodal diffusion mechanism²⁴.

Fig (4) shows the representative SEM micrographs of the as prepared Zn substituted Li-Cu ferrite. It has been seen from the micrograph that the dense microstructures are obtained for all the samples It indicates that the ferrite particles obtained by this method having agglomeration to some extent due to the relative microwave sintering and interaction between magnetic particles. The values of grain diameter are given in Table. I

Sr No	Composition	Grain Size with chemical reaction temperature		
51.100		100 °C(nm)	125 °C(nm)	150 °C(nm)
1	X=0.05	90	68.1	63
2	X=0.1	78	64	62
3	X=0.15	65	59.9	55
4	X=0.2	68	58	43
5	X=0.25	42	65	53
6	X=0.3	45	80.5	63.25

Table 1 Grain Size for Different Chemical Reaction Temperature

The particle sizes of the samples prepared at 100 °C are in the range 42 nm to 90 nm. It can be found from fig (4) that the particle size of Zn substituted ferrites are increases with increase in Zn concentration and the particles are in slightly agglomerated state which may be beneficial towards having good packing density of the material leading to higher bulk capacity ²⁵.







Fig. 1 - IR absorption spectra for chemical reaction temperature $100^{\circ}C$



Fig. 2 - IR absorption spectra for chemical reaction temperature 125°C

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Fig. 3- IR absorption spectra for chemical reaction temperature 150^{0} C

		Temperature=100 °C	Temperature=125 °C	Temperature=150 °C
1	X=0.05			
2	X=0.1			





3	X=0.15	ALCON DE LA LA CONTRACTÓN DE LA CONTRACTÓN	
4	X=0.2		
5	X=0.25		
6	X=0.3		

Fig.4-SEM micrograph of samples

The considerable increase in grain size with composition prepared at 100 °C shows the onset of nonuniform grain growth. The grain growth may be due to the formation of larger amount of liquid phase in the samples. The exaggerated grain growth hinders the migration of the pores to the grain boundary and hence, contributes to the reduction of the density 26 .

Sample prepared at 125°C and 150°C shows decrease in grain size with composition Zn content for X = 0.25, 0.2, 0.15 and again increase with increase in zn concentration for X=0.05, 0.1. The grain growth behaviour is compromised between the driving force for grain boundary movement and retarding force by pores. During the microwave combustion process, a force is generated due to thermal energy, which drives the grain boundaries to grow over pores thereby decreasing the pore volume and making the material dense. When the driving force of the grain boundary for each grain homogeneous, the sintered





body attains uniform grain size distribution and unless homogeneous, abnormal grain growth occurs. Further, the strength of the driving force depends upon diffusivity of individual grains, sintering temp and porosity ²⁷. Therefore, the smaller values of grain size for X = 0.25, 0.2, 0.15 could be due to more porosity since the pores neutralize the driving force it also confirmed by veisser et al ²⁸. For X = 0.05 and X=0.1, it gives greater grain size because of the effect of non- magnetic grain boundary. The composition shows the decrease in grain with increase in temperature of synthesis x = 0.25, x=0.3 shows greater values of grain size when it is prepared at reaction temp 125 °C and lower values at 100°C and 150°C. Similar values of grain size are reported by Chang Sun et.al ²⁹. Microwave combustion activates the sintering and increases the density. The behaviour of grain growth reflects the competition between the driving force for grain boundary movement and the retarding force expected by pores.

This can be attributed to the chemical kinematics it was found that the rates of most of the chemical reactions increase with increase in temperature therefore it has been found that the temperature 100°C, 125°C and 150°C have effect on the phase structure, morphologies, grain growth and grain boundaries.

Conclusions

- i) Li-Zn-Cu ferrite samples with different composition have been prepared using microwave assisted combustion method
- ii) The IR spectra confirmed the formation of spinel structure and gave information about the distribution of ions between the two sites, tetrahedral (A) and octahedral (B).
- iii) SEM gives the grain size in the 45 nm to 90 nm. The reaction temperature can be exploited for the production of fine magnetic powder of various sizes.

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