STRUCTURAL CHARACTERIZATION AND ELECTRICAL PROPERTIES OF $ZnFe_2O_4$ SPINEL FERRITE

May Thwe Soe[1] and Myat Shwe Wah[2]

Abstract

Zinc ferrite, $ZnFe_2O_4$, has been prepared by solid state reaction method at 1150 °C for 5 h in vacuum chamber (160 mmHg). Analar (AR) grade zinc oxide, ZnO, and ferric oxide, Fe_2O_3, were used to prepare and characterize for the sample. The as-prepared $ZnFe_2O_4$ sample was characterized by XRD methods. XRD pattern reveals that the sample belongs to spinel type cubic structure and the lattice parameters of the sample are obtained as a = b = c = 8.86 Å respectively. Crystallite size of the sample is also obtained as 46.06 nm. Variation of the electrical conductivity and dielectric constant with temperature were studied by electrical resistance and capacitance measurements. The electrical conductivity results show that the sample is a superionic conductor or fast ion conductor at high temperature ($T \geq 523$ K).

Keywords: Zinc Ferrite ($ZnFe_2O_4$) Spinel, Zinc Oxide (ZnO), and Ferric Oxide (Fe_2O_3), electrical conductivity and dielectric constant

Introduction

There are various types of microwave absorbers such as dielectric absorbers, magnetic absorbers, resonant absorbers and hybrid absorbers. Ferrites are preferred as microwave absorbers for portable wireless devices operating in the microwave band because they are compact, light weight, less costly and can be easily developed. In view of its several potential applications, a zinc spinel ferrite, ZnF_2O_4 microwave absorber has been developed and characterized for use in the 2.4 GHz ISM band. Zinc ferrite ($ZnFe_2O_4$) having a cubic spinal structure is a soft magnetic material and is widely studied as microwave absorbing material. In the present work, the compound of zinc spinel ferrite, $ZnFe_2O_4$, was prepared by conventional solid state reaction method and characterized by XRD, electrical conductivity and dielectric measurements to study the structural, microstructural, vibrational, thermal and electrical properties of the sample.

Materials and Method

In this chapter, the main constituents of the present experimental work include the sample preparation of the zinc ferrite, $ZnFe_2O_4$ spinel, structural analysis by powder X-ray diffraction measurement, electrical conductivity and dielectric constant measurements of the $ZnFe_2O_4$ spinel.

Preparation of Zinc Ferrite, $ZnFe_2O_4$

The raw materials used for the preparation of samples are conventional oxides. The candidate material of zinc ferrite, $ZnFe_2O_4$, was prepared by solid state reaction method. The preparation of sample includes the following steps:

(i) weighing the starting materials,

(ii) mixing, grinding,

(iii) pumping, and annealing

(iv) characterizing.

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The starting materials of Analar (AR) grade zinc oxide, ZnO, and ferric oxide, Fe_2O_3, were weighed with stoichiometric composition to prepare, $ZnFe_2O_4$. The mixture powder was ground by an agate motor for 1 h to be homogeneous and to obtain fine grain samples. The powder was annealed at 1150 °C for 5 h in vacuum chamber (160 mmHg) by using DELTA A SERIES temperature controller. The K-type thermocouple was used as the temperature senso. Finally, the candidate material of $ZnFe_2O_4$ spinel was obtained. The procedure for the preparation of zinc ferrite is described by the flow chart in Figure 2.

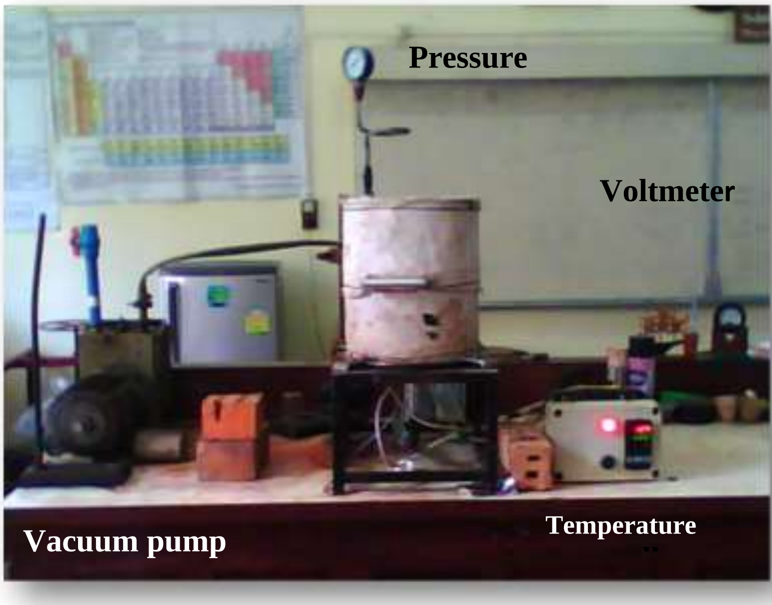

Figure 1 Photograph of the experimental setup of sample preparation system

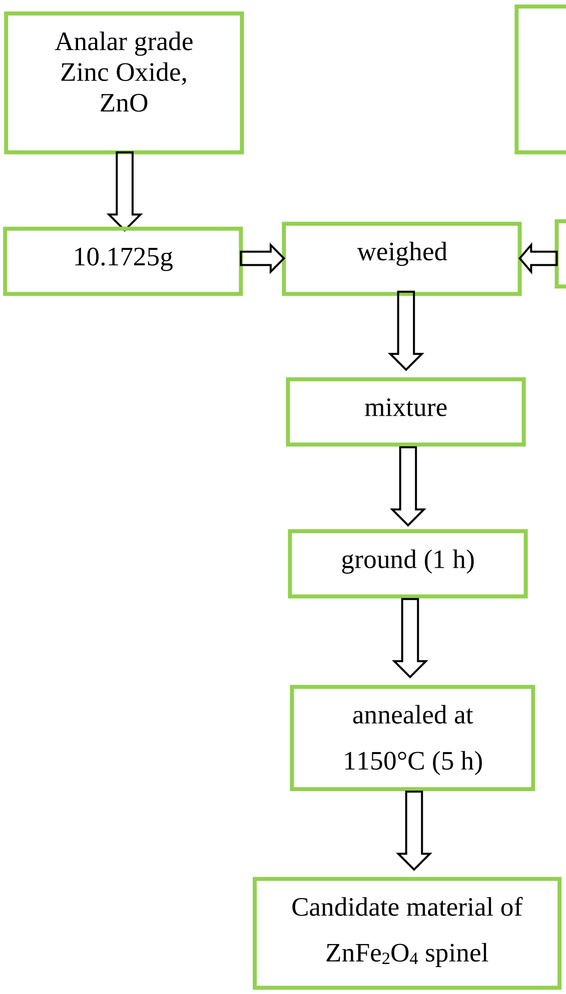

Figure 2 Procedure for the preparation of zinc ferrite

Electrical Conductivity and Dielectric Constant Measurement

The electrical conductivity and dielectric constant of the pelletized $ZnFe_2O_4$ sample were investigated in the temperature range 300 K (27 °C) - 923 K (650 °C) by using CAHO SR-T903 Temperature Controller. The diameter and thickness of the sample were used as 1.20 cm and 0.17 cm respectively. The dimensions of the sample were measured by using Digital Vernier Caliper (Taiwan). Firstly, the sample was fixed on glass plate and silver contacts were made over the sample to ensure good electrical contacts to measure the electrical properties such as resistances that change with temperatures. Of course, the surfaces of the palletized sample (sample surfaces) and electrodes (copper plates) are not optically homogeneous, But, in practice, the surfaces of the sample and electrodes must be homogeneously contacted with each other when the light or temperature dependence measurements of electrical parameters, such as resistance, capacitance and voltage of the samples. Thus, silver paste (electrical and thermal conducting paste) was used to interface or homogeneously contacted between surfaces of crystal and electrodes. Electrical conductivity measurements were made on the sample in a stainless-steel conductivity cell in which the sample is maintained by a spring-loaded support between copper leads using two polished Cu disc as electrodes.

The temperature sensor of K-type thermocouple (up to 1073 K) was placed near the sample to record real temperatures throughout the measurement. The copper block holder (heater chamber) was heated by using the four of 300W heater coils. The electrical resistances and capacitances of the samp1e were measured by using FLUKE 45 Dual Display digital multimeter and FUKE DM6013A Digital CAPACITANCE METER with heat conduction technique. The electrical conductivity of ionic crystals have been calculated by using the formula

$$\sigma = \frac{t}{R\,A}$$

where,

t = the thickness of the sample or the distance between the two electrodes
A = the cross-sectional area of the electrodes or sample
R = the resistance of the sample

Photograph of the experimental setup of electrical conductivity measurement is shown in Figure 3. The dielectric constants have been calculated by using the formula

$$\varepsilon_r = \frac{C\,t}{\varepsilon_0 A}$$

where,

C = the capacitance
t = the thickness
ε_0 = the permittivity of free space (8.8541 x 10^{-12} F)

Figure 3 Photograph of the experimental setup of electrical resistance and capacitance measurement

Characterization of $ZnFe_2O_4$

This research work describes the experimental results and discussion of structural and electrical characteristics of zinc ferrite, $ZnFe_2O_4$ from the measurements of XRD and electrical conductivity measurements.

Results and Discussion

Structural Analysis by XRD

X-ray diffraction data were collected from powder samples of the zinc ferrite, $ZnFe_2O_4$ using a PC-controlled RIGAKU MULTIFLEX automated X-ray diffractometer with monochromatic CuK_α (λ=1.54056 Å) using Ni-filter (scan speed 4º/min). The Nal(Tl) scintillation counter was used to detect the diffracted X-ray from the sample. The measurement was taken from 10 º to 70 º with 2θ diffraction angle. Lattice parameters were determined from the indexed data using experimental results of low angle reflections.

Powder X-ray diffraction pattern of $ZnFe_2O_4$ spinel is shown in Figure 4. The collected XRD data were compared to those of JCPDS data library to identify the collected XRD pattern of sample. Most of the collected diffraction lines were assigned by JCPDS. Some of the diffraction lines (e.g, 2θ is 24.18 º) were not assigned with JCPDS files due to small crystallite effects, crystal defects or chemical heterogeneity of the samples. In this XRD pattern, the diffraction line at 33.30 º or (311) plane is found to the strongest among all lines and it indicated the (311) peak is dominated in the as-grown polycrystalline $ZnFe_2O_4$ spinel. Some of the XRD data of diffraction angle (2θ), atomic spacing (d), miller indices (hkl), full width at half maximum (FWHM) and peak height of the sample are tabulated in Table 1.

According to XRD pattern, zinc ferrite, $ZnFe_2O_4$ belongs to spinel type cubic structure at room temperature. The lattice parameters were evaluated by using crystal utility of the equation of

$$\frac{\sin^2\theta}{(h^2+k^2+l^2)} = \frac{\lambda^2}{4a^2}$$

Lattice parameters of the sample are a = b = *c* = 8.86 Å. From the observed XRD data, the crystalline size of the $ZnFe_2O_4$ was estimated by using the Scherrer formula,

$$t = \frac{0.9\lambda}{B\cos\theta}$$

where,

t = the crystallite size (nm)

λ = the wavelength of incident X-ray (nm)

θ = the diffraction angle of the peak under consideration at FWHM (º)

B = the observed FWHM (radians)

In this work, we used the diffraction line 2θ is 33.30 º. Miller index (hkl) is (311) and FWHM is 0.18 º to calculate the crystallite size of the sample because this line is the strongest in intensity among the observed XRD pattern. The crystallite size of the sample was obtained as 46.06 nm.

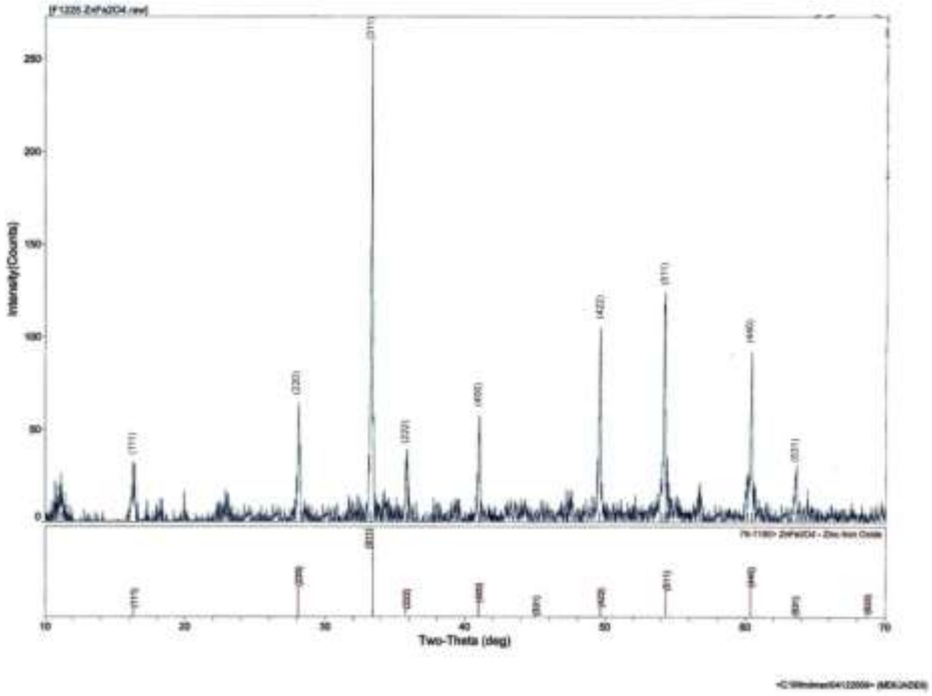

Figure 4 XRD pattern of zinc ferrite, $ZnFe_2O_4$

Table 1 Powder XRD data of zinc ferrite, $ZnFe_2O_4$

Line No.	2θ (º)	(hkl)	d (Å)	FWHM (º)	Intensity (%)
1	16.18	(111)	7.95	0.23	9.50
2	28.04	(220)	3.15	0.15	24.00
3	33.30	(311)	2.69	0.18	100.00
4	35.79	(222)	2.51	0.14	14.70
5	41.02	(400)	2.20	0.12	21.40
6	49.60	(422)	1.84	0.15	40.50
7	54.41	(511)	1.69	0.09	43.90
8	62.27	(440)	1.49	0.16	25.10
9	63.71	(531)	1.45	0.13	7.20

The electrical conductivities of the sample at 300 K (starting temperature) and 773 K (temperature of superionic conductivity state) are obtained as 5.3653×10^{-9} S cm^{-1} and 1.4414 $\times 10^{-5}$ S cm^{-1} respectively. The experimental data are tabulated in Table 2. As presented in Table 1, the electrical conductivity of the sample at T ≥ 773K is found to be ~ 10^{-5} S cm^{-1} that shows the superionic conductivity of the sample. Thus, the sample is a superionic conductivity of the sample. Thus, the sample is a superionic conductor or fast oin conductor at high temperature (T ≥ 773 K).

If a material contains polar molecules, they will generally be in random orientations when no electric field is applied. An applied electric field will polarize the material by orienting the dipole moments of polar molecules. This decreases the effective electric field between the plates and will increase the capacitance of the parallel plate structure. The dielectric constant is the relative permittivity of a dielectric material. It is an important parameter in characterizing capacitors. The capacitance of a set of charged parallel plates is increased by the insertion of a dielectric material.

In the present work, variation of the dielectric constants with temperatures of $ZnFe_2O_4$ sample in the temperature range 300 K – 923 K is shown in Figure 5. The dielectric constants of the sample are found to linearly increase with increasing temperatures. As shown in (ε_r-T) relationship, the slope of the curve is found to linear type and that indicates any phase changes characters are not occurred in the sample due to thermal agitation. It can be said that the sample is a thermally stable or thermally inert material.

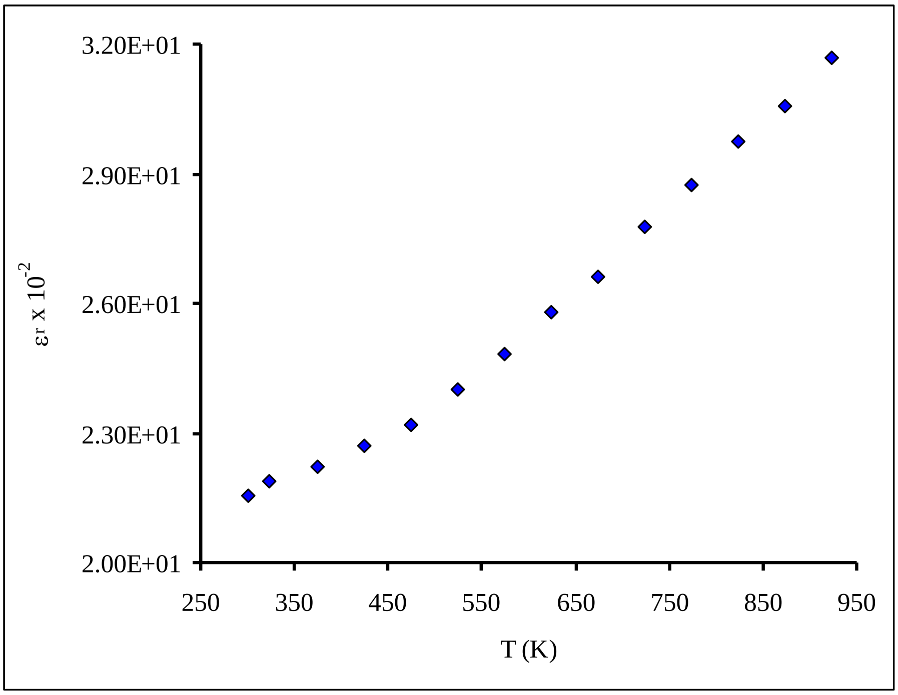

Figure 5 Plot of the variation of dielectric constants with temperatures of $ZnFe_2O_4$

Table 2 Experimental data of electrical conductivity and dielectric constant measurements of $ZnFe_2O_4$

T (K)	1000/T (K^{-1})	R (kΩ)	σ (S cm^{-1})	ln σ	ε_r	$\varepsilon_r \times 10^{-2}$
300	3.3333	27000.00	5.3653E-09	-19.0433	2.16E+03	2.16E+01
323	3.0960	18150.00	7.9815E-09	-18.6461	2.19E+03	2.19E+01
373	2.6810	8560.00	1.6923E-08	-17.8946	2.22E+03	2.22E+01
423	2.3641	2630.00	5.5081E-08	-16.7145	2.27E+03	2.27E+01
473	2.1142	920.00	1.5746E-07	-15.6641	2.32E+03	2.32E+01
523	1.9120	560.00	2.5869E-07	-15.1677	2.40E+03	2.40E+01
573	1.7452	408.00	3.5506E-07	-14.8510	2.48E+03	2.48E+01
623	1.6051	120.00	1.2072E-06	-13.6272	2.58E+03	2.58E+01
673	1.4859	76.50	1.8936E-06	-13.1770	2.66E+03	2.66E+01
723	1.3831	37.50	3.8630E-06	-12.4641	2.78E+03	2.78E+01
773	1.2937	10.05	1.4414E-05	-11.1473	2.88E+03	2.88E+01
823	1.2151	5.25	2.7593E-05	-10.4979	2.98E+03	2.98E+01
873	1.1455	4.40	3.2924E-05	-10.3213	3.06E+03	3.06E+01
923	1.0834	4.25	3.4086E-05	-10.2866	3.17E+03	3.17E+01

Conclusion

Zinc ferrite, $ZnFe_2O_4$ was prepared by solid state reaction method. Structural, microstructural, vibrational and thermal characteristics of the sample were studied by XRD methods. The electrical conductivities and dielectric constants of the sample were investigated in the temperature range 300 K - 923 K. Powder XRD pattern indicates that the $ZnFe_2O_4$ spinel belongs to cubic structure and the lattice parameters of the sample are obtained as $a = b = c = 8.86$ Å respectively. The crystallite size of the sample is also obtained 46.06 nm. The electrical conductivities of the sample at 300 K and 773 K are obtained as 5.3653×10^{-9} S cm^{-1} and 1.4414×10^{-5} S cm^{-1} respectively. The activation energy is obtained as 0.3530 eV. The sample is a superionic conduction or fast ion conductors at the temperature $T \geq 773$ K. From the (ε_r-T) relationship, the dielectric constants of the sample are increased with increasing temperatures. The slope of the (ε_r-T) graph is found to linear and it indicates any phase changes are not occurred. According to experimental result, $ZnFe_2O_4$ spinel can be considered as the solid electrolyte materials or first ion conductors at high temperatures.

Acknowledgements

I would like to thank Professor Dr Maung Maug Shwe, PhD (YU), Head of Department of Physics, Professor Dr Myat Shwe Wah, PhD (YU) and Professor Dr Zay Ya Aung, PhD (YU), West Yangon University, for their kind permission to carry out this paper.

References

Banwell C.N. & Mc Cash E.M., (1994) *Fundamentals of Molecular Spectroscopy*

Bolton W., (1991) *Instrumentation & Measurement* (Oxford: Newnes)

Callister W.D. (2001) *Fundamentals of Materials Science and Engineering* (New York: Wiley)

Candeia R.A., et al (2004) *Materials Letters* 58 569

Cullity B.D. (1978) *Elements of X-Ray Diffraction* (Reading: Wesley)

Goldstein et al, (1981) *Scanning Electron Microscopy and X-Ray Microanalysis Manuals*

Hollas J.M., (2004) *Modern Spectroscopy* (New York: Wiley)

Iqbal M.J. (2009) *Lecture on Synthesis and Characterization of Nanostructured Spinel Ferrites* (Islamabad: Quaid – i-Azam University)

Kakirda A., et al (2008) *Bulletins Materials Science* 31 (5) 767

Kanagadurai R. et al (2009) *E Journal of Chemistry* 6 (3) 871

Li D. S., Harikawa T., Liu J. R., Itoh M., and Machida K., (2006) *J Alloys Compd* 408 1429

Li Z. W., Yang Z. H. and Kong L. B. (2010) *Journal of Applied Physics* 108 063927

Liu J. R., Itoh M., and Machida K., (2006) *Appl Phyu Lett* 88 062503/1.

Masala O., Haffman D., Sundaram N., Page K., Proffen T., Lawes G., and Seshadri R., (2006) *Solid State Sci* 8 1015.

Moulson A.J. & Herbert J.M. (1997) *Elefctroceramic Materials, Properties & Applications* (London: Chapman & Hall)

Nell J. & Wood B.J. (1989) *American Mineralogist* 74 1000

Peng C.H., Hwang C.C, Wan J., Tsai J.S., and Chen S.Y., (2005) *Mater Sci Eng* B 117

Pillai S.O., (2006) *Solid State physics* (New Delhi: New Age)

Qiu J.X., Wang C.Y., and Gu M.Y., *Master Sci Eng* B 112 (2004) 1.

Ross S.D. (1972) *Inorganie Infrared and Raman Spectra* (London: Me Graw-Hill)