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Microwave hydrothermal synthesis of nanosize Ta_2O_5 added Mg-Cu-Zn ferrites

T. KRISHNAVENI, S. R. MURTHY
Department of Physics, Osmania University, Hyderabad 500 007, India
E-mail: ramanasarabu@yahoo.com

F. GAO, Q. LU, S. KOMARNENI
Materials Research Institute, Pennsylvania State University, University Park, PA 16802, USA

Tantalum oxide added MgCuZn ferrite powders were synthesized by a co-precipitation method using NaOH in a microwave-hydrothermal (M-H) apparatus. The phase identification of the prepared samples was done by X-ray diffraction and crystal size and morphology were determined by transmission electron microscopy (TEM). Nano-phase ferrites with high surface area were synthesized at 160°C after a treatment time of 1 hour. The M-H synthesized powders were conventionally sintered at a temperature of 900°C/4h. The variations of the sintered density, initial permeability and electrical resistivity as a function of additive concentration at room temperature have been investigated.

1. Introduction

Synthesis of nano sized spinel ferrite particles has become an interesting field of modern ceramic research. These nano-sized particles can be prepared by various methods like hydrothermal, microwave-hydrothermal, co-precipitation, combustion, sol-gel, precursor, spray drying and freeze drying, micro emulsion, reverse micelle method etc. [1–3]. Out of all methods available, the microwave hydrothermal (M-H) method is one of the promising methods for preparing fine ceramic powders [4–6]. The main advantages of microwave hydrothermal method over the conventional hydrothermal method are: the kinetics of the reaction is enhanced by one to two orders of magnitude, novel phases can be obtained and the rapid heating to treatment temperature saves time and energy. Komarneni *et al* [6] have used the M-H method to prepare nano-sized powders of various ceramics with high surface area.

MgCuZn ferrite is one of the important magnetic materials for many high frequency applications. This is because of its better properties at higher frequencies (high resistivity, high Curie point, environmental stability, low cost) and lower densification temperature than that of presently used NiCuZn ferrite [7–9]. Therefore, in the present investigation, a detailed investigation has been made on Ta_2O_5 added MgCuZn ferrites. These ferrites were prepared using the nano-ferrite powders synthesized using the microwave hydrothermal (M-H) method. Room temperature electrical and magnetic properties were measured on sintered ferrite and results obtained are presented in this paper.

2. Experimental method

Pure chemicals of magnesium nitrate [$Mg(NO_3)_2{\cdot}6H_2O$], copper nitrate [$Cu(NO_3)_2{\cdot}3H_2O$], zinc nitrate [$Zn(NO_3)_2{\cdot}6H_2O$)] and iron nitrate [$Fe(NO_3)_2{\cdot}9H_2O$] were mixed according to molar ratio to obtain the composition $Mg_{0.2}Cu_{0.3}Zn_{0.5}Fe_20_4$. Tantalum oxide was added in the amounts of 0 (sample 1), 0.2 wt% (sample 2), 0.4 wt% (sample 3), and 0.6 wt% (sample 4). Then the powders were dissolved in de-ionized water and tantalum oxide [Ta_2O_5] was added followed by the adjustment of pH to 10 with NaOH. The mixture was then treated in a Teflon lined vessel using a microwave accelerated reaction system (MARS-5, CEM Corp., Mathews, NC). This system uses 2.45 GHz microwaves and can operate at 0–100% full power (630 ± 50W). The system is controlled by temperature and can attain a maximum of 240°C. In the present investigation all the samples were synthesized at 160°C for 1 hour. The reaction vessel was connected to an optical probe that monitored and controlled the temperature during synthesis. The products obtained were filtered, and then washed repeatedly with de-ionized water, followed by drying in an oven overnight. The prepared powders

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were weighed and the percentage yields were calculated from the expected and the amount that was actually crystallized.

All the synthetic products were characterized by using powder X-ray diffraction. Particle size and morphology were determined using transmission electron microscopy (TEM)(Model JEM-2010, JEOL, Tokyo, Japan). Infrared spectra (IR) were recorded using a Nicolet DTGS TEC detector spectrophotometer from 1500 to 400 cm^{-1} by the KBr pellet method.

The nanoferrite powders were mixed with an appropriate amount of 2 wt% polyvinyl alcohol as a binder. Then the powders were pressed at a pressure of 1500 kg/cm^2 to for pellets and toroidal specimens. After binder was burnt out at 600°C/2 h the compacts were conventionally sintered at 900°C/4 h in air. The permeability and dielectric properties at room temperature were measured using Agilent Technologies 4291B impedance analyzer.

3. Results and discussion

The X-ray diffraction (XRD) patterns of the as synthesized Ta_2O_5 (0.0, 0.2, 0.4, 0.6 wt%) added MgCuZn ferrite powders are shown in Fig. 1. It can be observed from the figures that extremely broad reflections are present, indicating fine particle nature of the material obtained.

TEM photographs of pure (Fig. 2a) and 0.6 wt% Ta_2O_5 (Fig. 2b powders revealed that particle size of the nano ferrites is ∼10–20 nm. The ferrites exhibited more or less spherical morphology and uniform size. Fig. 3. Shows the IR spectra for the samples under investigation. It can

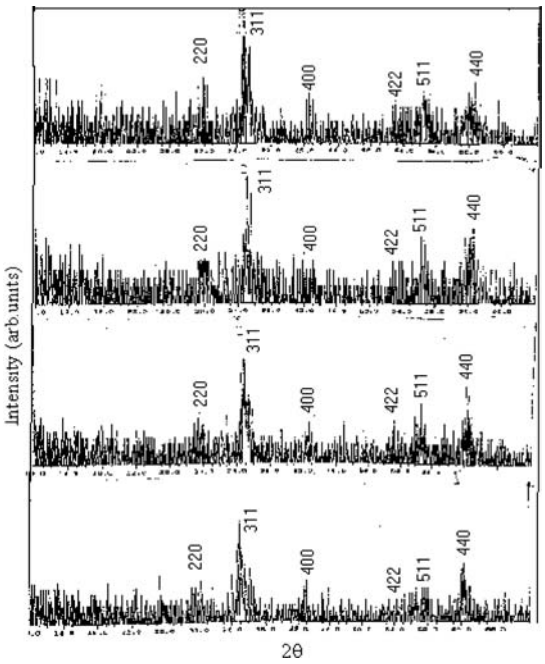
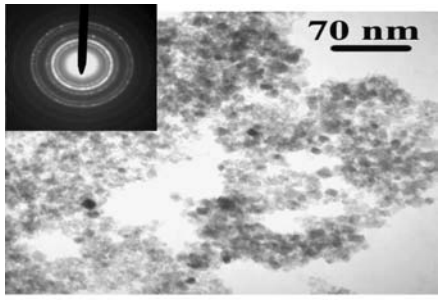
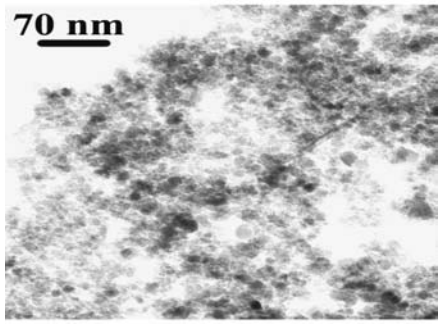


Figure 1 XRD Patterns of the as synthesized powders of MgCuZn ferrites.



(a)



(b)

Figure 2 (a) TEM picture of Pure and (b). 0.6 wt% Ta_2O_5 addedMgCuZn ferrite.

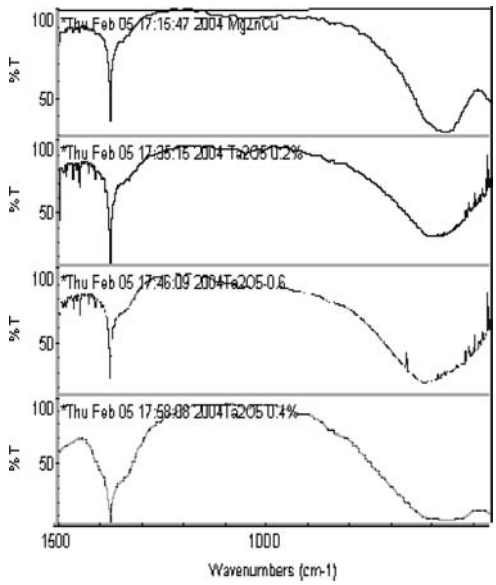


Figure 3 IR spectra for the as-synthesized nanosize powders of Ta_2O_5 added MgCuZn ferrites.

be observed from the figure that two bands are in the range of 400–1000 cm^{-1}; the high frequency band (ν_1) is in the range 550–600 $cm^{-1}$and the low frequency band (ν_2) is 410–420 cm^{-1}. These bands are common features for all the ferrites. The vibrations of the unit cell of the cubic spinel can be constructed in the tetrahedral (A-)

site and OCtahedral (B-) site. So, the absorption band ν_1 is caused by the stretching vibration of the tetrahedral metal-oxygen bond, and the absorption ν_2 is caused by the metal-oxygen vibrations in octahedral sites. The shifting of bands towards higher frequency is attributed to the decrease in the unit cell dimensions. The increase in the frequency of the absorption bands is attributed to the creation of lattice vacancies. These vacancies retard the vibration of octahedral and tetrahedral groups [11, 12]. The slight variation in ν_1 and ν_2 indicate small changes in their composition. The band at 1388 cm^{-1} corresponds to NO_3^- stretching vibration. This band disappeared after the sintering of the powders.

Bulk densities (d_x) of the sintered samples are measured using Archimedes' principle and obtained values are given in Table I. It can be observed from the table that the bulk density increases with an increase of Ta_2O_5 from 92 to 97% of theoretical density. The bulk densities of the present samples are compared with conventionally prepared [10] samples in Fig. 4. From the figure it is clear that the bulk density is affected by the initial particle size of the powders.

Fig. 5 gives the XRD patterns for the sintered ferrites. It can be seen from the figures that all the samples are mono-phase in nature and posses spinel structure. Using the XRD data, the values of lattice constants (a_0) were calculated. The values of lattice constants increase from 8.3995 Å to 8.4051 Åwith an increase of Ta_2O_5 (0 to 0.6 wt%) in MgCuZn ferrites. This increase may be attributed to the presence of a few Ta^{+5} ions in the substitution or

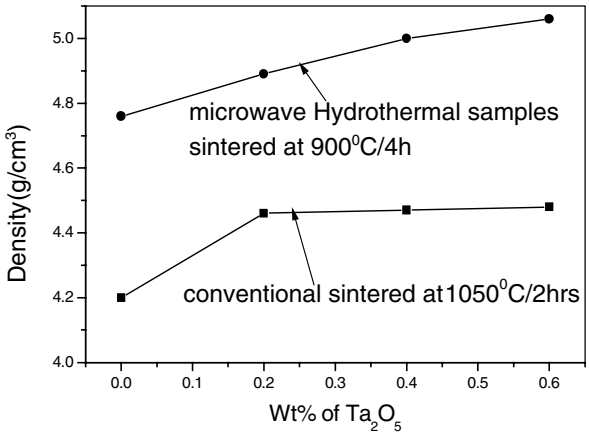


Figure 4 Comparison of Bulk densities of the MgCuZn ferrites.

TABLE I Data for the MgCuZn ferrites

Sample no	wt % of Ta_2O_5	a_0 (Å)	D_x (g/cm^3)	d_x (g/cm^3)	Porosity (%)
1	0.0	8.3995	5.22	4.76	8.62
2	0.2	8.4018	5.20	4.89	6.02
3	0.4	8.4032	5.19	5.02	3.85
4	0.6	8.4051	5.18	5.06	2.62

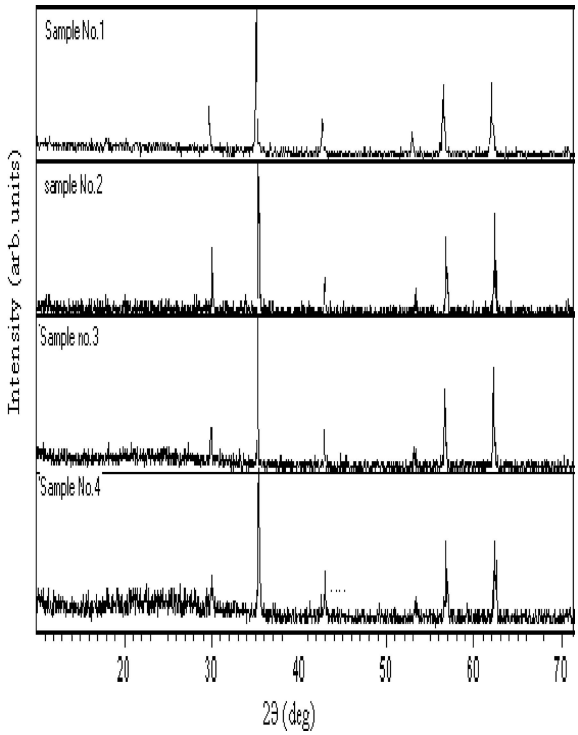


Figure 5 XRD patterns of the sintered MgCuZn ferrites.

interstitial positions in the host spinel lattice. Using the lattice constant data the value of X-ray density (D_x) has been estimated and obtained values are presented in the Table I. Using the X-ray and bulk densities data, the value of porosity was estimated. The porosity for the samples varies from 9% to 3%.

The permeability and dielectric properties for the present samples were measured at room temperature for the frequency of 1 MHz. Table II gives the values of initial permeability (μ_i), Dielectric constant (ε), Dielectric loss (tan δ) measured at 1 MHz and the room temperature d.c.resistivity (ρ), Saturation Magnetization (σ_S) for all the sintered ferrite samples.

It is observed from the table that the value of d.c.resistivity decreases with the addition of 0.2 wt% Ta_2O_5. However, with further addition of Ta_2O_5 the value of ρ is found to increase. This behavior can be understood by the mechanism proposed by Yamamoto *et al.*

TABLE II Room temperature data for the MgCuZn ferrites

		(measured at 1 MHz)			($A-m^2/Kg$)
Sample no.	$\rho \times 10^7$ (Ω-cm)	ε	tan δ	μ_1	σ_s
1	8.6	12	0.05	1087	58.62
2	4.0	14	0.05	1670	63.79
3	2.5	12	0.05	1321	64.96
4	6.3	13	0.05	1141	66.48

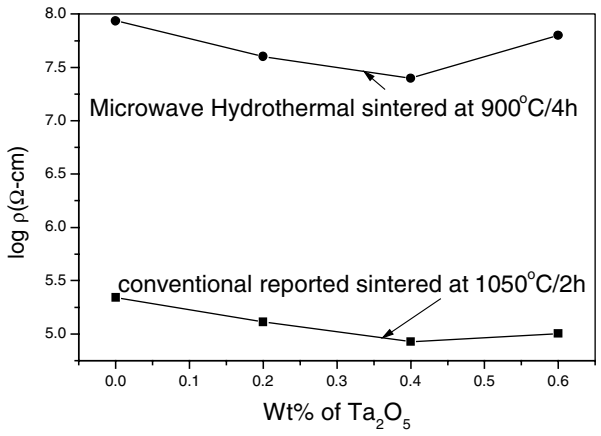


Figure 6 Comparison of room temperature d.c. resistivities of the MgCuZn ferrites.

[13], the decrease of ρ in the Ta_2O_5 doped ferrites should be closely related to the creation of the cation vacancies to maintain the electrical neutrality. These vacancies lead to the increase of the electrons as a result of dissociation of oxygen in the vicinity of cation vacancies.

The d.c. resistivity of the present samples is also compared with the values from the literature and is shown in Fig. 6. It can be observed from the figure that the d.c. resistivity has been increased by an order of two.

From the table, it can also be observed that the addition of Ta_2O_5 has no pronounced effect on dielectric constant and the dielectric loss properties of the MgCuZn ferrites and they almost remain constant. It can be also observed that the values of initial permeability values increase for 0.2 wt% addition but decrease sharply on further additions and for 0.6 wt% the value approaches the pure samples values.

The values of saturation magnetization (σ_S) measured at room temperature using VSM for all the samples are also presented in the Table. II. From the table one can observe that the value of σ_S increases with the addition of Ta_2O_5 and the value is maximum for 0.6 wt% sample.

4. Conclusions

Ta_2O_5 added MgCuZn ferrite powders were successfully prepared using Microwave hydrothermal method at a temperature of 160°C/1 h. The obtained powders were characterized using the XRD, TEM and IR spectroscopy. Fine nano powders of about 10–20 nm were obtained. The properties such as bulk density, resistivity, permeability and saturation magnetization are found to be higher for 0.6 wt% Ta_2O_5 added MgCuZn ferrite.

The sintered samples show high density at a low temperature of 900°C as compared with the available values with the literature. The d.c. resistivity of the present samples is two orders more than that the available reports.

Acknowledgements

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References

1. X. YI, Q. YITAI, L. JING, CHENZUYAO and YANG LI, *Mat. Sci. Eng.* **B 34** (1995) L1.
2. W. C. KIM, S. J. KIM, S. W. LEE, C.S. KIM, *J. Magn. Magn. Mater.* **226** (2001) 1418.
3. H. W. WANG and S.C.KUNG, *J. Magn. Magn. Mater.* **270** (2004) 230.
4. S. KOMARNENI, R. ROY and Q.-H. LI, *Mater. Res. Bull.* **27** (1992) 1393.
5. S. KOMARNENI, Q-. LI, K. STEFANSON and R. ROY, *J. Mater. Res.* **8** (1993) 3176.
6. S. KOMARNENI, M. C. D'ARRIGO, C.LEONELLI, G.C. PELLACANI and H. KATSUKI, *J. Amer. Ceram. Soc.* **81** (1998) 3041.
7. S. R. MURTHY, *Bull. Mater. Sci.* **24** (2001) 379.
8. N. REZLESCU, E. REZLESCU, L. REZLESCU, P. D. POPA, C. PANISCU and M.L. CRAUS, *Mater. Res. Bull.* **33** (1998) 915.
9. N. REZLESCU, E. REZLESCU, L. REZLESCU, P. D. POPA, C. PANISCU and M.L. CRAUS, *J. Magn. Magn. Mater.* **182** (1998) 199.
10. N. REZLESCU, L. REZLESCU, P. D. POPA, C. PANISCU and L. SAHALARIE, *Cryst. Res. Technol.* **36** (2001) 157.
11. B. K. LABDE,M. C. SABLE and N. R. SHA MKUWAR, *Mater. Lett.* **57** (2003) 1651.
12. Z. YUE, L. LI, J. ZHOU, H. ZHANG and Z. GUI, *Mater. Sci. Eng.* **B64**(1999) 68.
13. Y. YAMAMOTO. A. MAKINO. and T. NIKAIDOU. in Proc. of 7th ICF, Bordeaux, September 3-6, 1996, edited by *J. Phys. IV France* **7** (1997) C1-121.

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