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

V. SEETHA RAMA RAJU*, 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

Lead oxide added Mg-Cu-Zn ferrite powders were prepared by a co-precipitation method in a microwave-hydrothermal (M-H) system. The synthesized ferrite samples were characterized by powder X-ray diffraction (XRD), Infrared spectroscopy (IR), transmission electron microscopy (TEM) and Differential scanning calorimeter (DSC). Nanophase ferrites (∼10–20 nm) with high surface area were synthesized at a low temperature of 160°C after a treatment time of 1 hour. The nano-powder was sintered at 900°C/4h in air atmosphere. The variations of the sintered density, electrical resistivity, initial permeability, and saturation magnetization with additive concentration have been investigated and the obtained results were compared with one prepared by the conventional ceramic method. It is found that the addition of PbO improves sintered density, electrical resistivity and permeability.

1. Introduction

It is well known that low temperature sintering of ferrites can be achieved by using ultra fine powders. The hydrothermal process is one of the promising methods for preparing fine ceramic powders among the wet chemical methods [1–3]. However, the hydrothermal method requires prolonged reaction time at a low temperature (below 200°C) to obtain the ferrite powders. For this reason, the introduction of microwave heating to the conventional-hydrothermal (C-H) method is advantageous for the synthesis of various ceramic powders, and this was named as microwave-hydrothermal (M-H) by Komarneni *et al*. [4].

The main advantages of this process over conventional-hydrothermal process are (a) the rapid heating to treatment temperature saves time and energy, (b) the kinetics of the reaction are enhanced by one to two orders of magnitude, (c) lead to the formation of novel phases, and (d) lead to selective crystallization. Komarneni et al [1–5] have used the M-H method to prepare nano-sized powders of various ferrites with large surface area. Hence, for the first time, in the present investigation M-H method was used for the preparation of nano-crystalline powders of MgCuZn ferrite.

From the survey of the literature, it was found that out of all ferrites available only NiCuZn ferrites are found to be dominant material for the use of MLCI. This is due to its better electro-magnetic properties [6–8]. Recently, it was found by us that MgCuZn ferrite is also a pertinent magnetic material for wide applications owing to its high resistivity, high Curie temperature, environmental stability and low cost [9]. It was also found that the value of initial permeability increased with decreasing the magnetostriction constant. The magnetostriction constant of MgCuZn ferrite is lower than that of NiCuZn ferrite and posses higher magnetic properties. Thus, further miniaturization of MLCI's is possible with MgCuZn ferrites than that of NiCuZn ferrites.

In high frequency applications for Mg-based polycrystalline ferrites porosity and resistivity are the main problems. These problems can be solved by addition of additives. The proper selection of additives will also promote low temperature sintering. The most commonly used additives are; the low melting compounds such as CaO, Na_2O, ZrO_2, PbO, Ta_2O_5 and V_2O_5 etc [10–12]. In the present investigation, additive chosen is PbO. In this paper we report on the synthesis, characterization and electrical properties of PbO added MgCuZn ferrites.

*Author to whom all correspondence should be addressed.
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2. Experimental method

Magnesium nitrate [$Mg(NO_3)_26H_2O$], Copper nitrate [$Cu(NO_3)_23H_2O$], Zinc nitrate [$Zn(NO_3)6H_2O$], Iron nitrate [$Fe(NO_3)_29H_2O$] and Lead nitrate [$Pb(NO_3)_26H_2O$] were dissolved in 50 ml of deionized water. The molar ratio of powders was adjusted to obtain composition $Mg_{0.2}$ $Cu_{0.3}$ $Zn_{0.5}$ Fe_2 O_4. The non-magnetic ions of PbO is added in the range from 0 (sample 1), 0.2 wt% (sample 2), 0.4 wt% (sample 3), and 0.6 wt% (sample 4). An aqueous NaOH solution was added to the prepared solution until the desired pH (∼9.12) value was obtained. The mixture was then treated in a Teflon lined vessel using a microwave digestion system (Model MDS-2000, 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 pressure and can attain maximum pressure of 200 psi, which is equivalent to 194°C, based on steam tables. In the present investigation all the samples were synthesized at 160°C. The reaction vessel is connected to a pressure transducer that monitors and controls the pressure during synthesis. The time, pressure and power were computer controlled. The products obtained were filtered, and then washed repeatedly with deionized water, followed by freeze-drying overnight. The prepared powders were weighted and the percentage yields were calculated from the expected total amount based on the solution concentration and volume and the amount that was actually crystallized.

All the synthesized powders were characterized using X-ray diffraction, Infrared spectra (IR) and Differential scanning calorimeter (DSC) techniques. IR spectra were recorded using a Nicolet DTGS TEC detector spectrophotometer from 1500 to 400 cm^{-1} by the KBr pellet method. DSC measurements were carried out on TA instrument to find out the possible decomposition temperature and phase changes that may occur in the samples.

Particle size and morphology were determined using transmission electron microscopy (TEM) (Model JEM-2010, JEOL, Tokyo, Japan). The surface area of ferrite samples was measured via multipoint BET nitrogen absorption method. In the present investigation ferrites with high surface ∼92 cm^2 were synthesized.

The obtained ferrite powders was mixed with 2wt% polyvinyl alcohol as a binder. Then the powder was uniaxially pressed at a pressure of 1500 kg/cm^2 to form pellet and toroidal shape specimens. The compacts were conventionally sintered at 900°C/4h in air atmosphere. The electrical properties such as the permitivity and permeability were measured using Agilent 4291B Impedance/Material analyzer.

3. Results and discussion

Fig. 1 shows the XRD patterns for all the synthesized powders under investigation. It can be seen from figure that phase-pure ferrites were obtained in all cases.

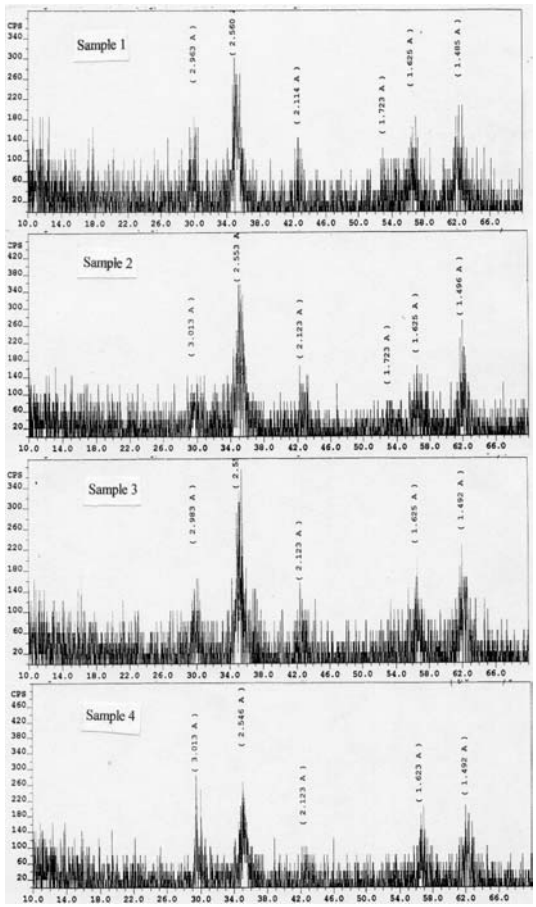

Figure 1 XRD patterns of M-H synthesized nano-phase PbO added MgCuZn ferrite powders.

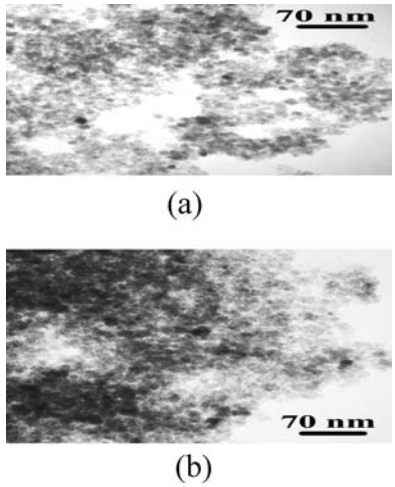

Figure 2 (a) .TEM pictures of PbO (0 wt %) and (b). (0.6 wt%) added MgCuZn ferrite.

TEM analysis revealed that nanophase ferrites ∼10–20 nm in size (Fig. 2a&b) could be synthesized at ∼160°C. These nanophase ferrites exhibited more or less spherical morphology and uniform size. Fig. 3 shows selected area electron diffraction ring pattern of the nanoparticles of MgCuZn ferrite. The ring pattern is well resolved

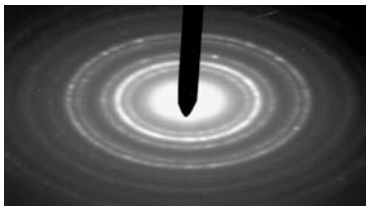

Figure 3 Selected area electron diffraction ring pattern of the nanoparticles of MgCuZn ferrite.

at (220), (311), (400), (422), (511), (440) reflections as in XRD pattern.

Fig. 4 shows the IR spectra for all samples under investigation. It can be observed from the figure that two bands are in the range of 400 to 1000 cm^{-1}, the high frequency band (ν_1) is in the range 550–580 cm^{-1} and the low frequency band (ν_2) is 410–420 cm^{-1}. These bands are common features for all 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 band ν_2 is caused by the metal-oxygen vibrations in octahedral sites. The shifting of bands towards high 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. The slight variation in ν_1 and ν_2 indicate that the method of preparation. The band at 1388 cm^{-1} corresponds to NO_3- stretching vibration. This band disappeared after the powders sintered [13–16].

All the samples are synthesized in the pH range of 8.95–9.45, and the yields of ferrites ranged from 85% to 95%. Proper control of the pH is the key factor in synthesizing phase-pure ferrites.

Fig. 5 shows the DSC graphs of few powder samples. It is evident from the graphs that a strong endothermic peak around 100°C is due to the removal of free adsorbed water molecules. The exothermic peak around 280°C can be attributed to the crystallization of the powder in to cubic phase and this temperature is the Curie temperature of the corresponding sample.

Fig. 6 gives the XRD patterns for the sintered ferrites. It can be seen from the figures that all the samples possess single phase in nature. Particle size for all the samples was estimated by Scherer's formula: $t = 0.9\lambda/B\cos\theta$, where t is the diameter of the crystal particle, $\lambda$is the wavelength of the target used (Cu K_α=1.5418 Å), B is the full width at half maxima of diffracted line in radian. The particle size thus obtained using the Scherer's formula of all the sintered samples is 80–95 nm.

Lattice parameter for all the samples was calculated using the XRD data and obtained data are presented in Table I. It can be see from the table that the values of lattice constants increases from 8.4404 Åto 8.4605 Å with an addition of PbO. This increase may be attributed to the presence of a few Pb^{+2} ions on the substitutional or interstitial positions in the host spinel lattice. Using the lattice constant data the values of X-ray density has been calculated and presented in Table I.

TABLE I Preparation data of the present samples

Sample No	Wt % of PbO	a_0 (Å)	D_x (g/cm^3)	d_x (g/cm^3)	Porosity (%)
1	0.0	8.4404	5.13	4.66	8.57
2	0.2	8.4503	5.11	4.76	6.85
3	0.4	8.4605	5.09	4.88	4.13
4	0.6	8.4702	5.08	5.02	1.18

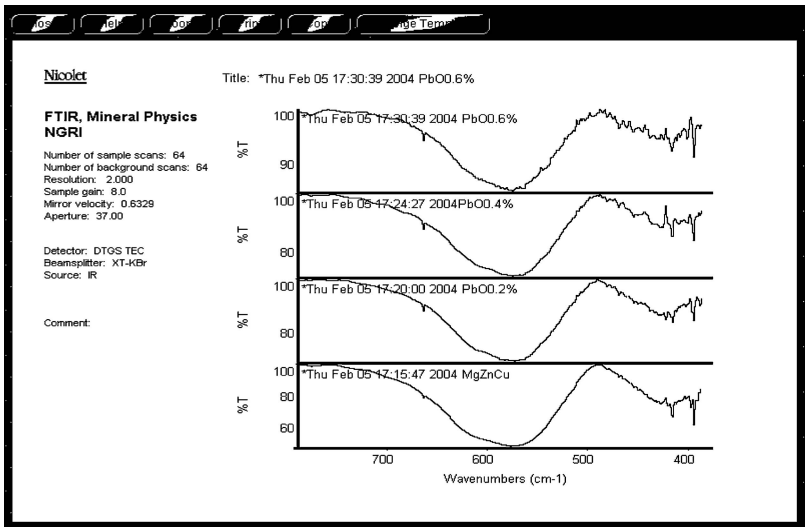

Figure 4 IR spectra for the nanosize powders of PbO added MgCuZn ferrites.

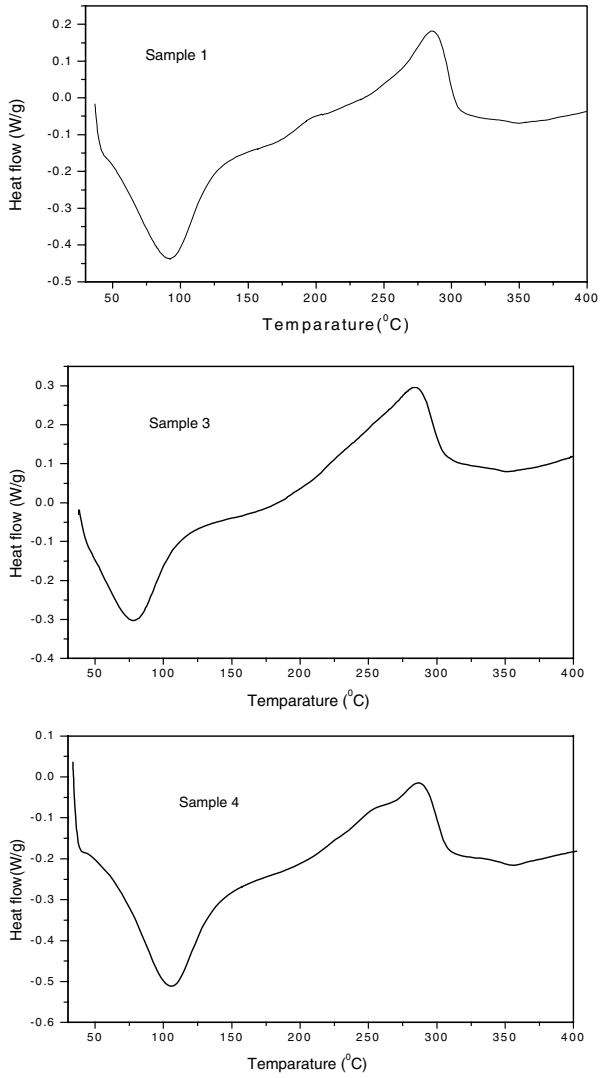

Figure 5 DSC graphs of few powder samples.

Table also gives values of the bulk density of the present samples. The bulk density of ferrite samples was measured using Arch medic's principle. It can be observed from the table that the addition of PbO leads to an increase in the bulk density. Higher density sample was obtained with an addition of PbO 0.6wt%. Using the X-ray density and bulk density data, the value of porosity was estimated and results are presented in Table I. Value of porosity is found to decrease with an addition of PbO.

Fig. 7 gives the comparison data of bulk density in the case of present samples and samples with same composition but prepared in the conventional solid-state route. Samples prepared by conventional method are sintered at 1100°C/8hr. It can be seen from the figure that the higher density samples were obtained at low sintering temperatures.

Table II gives the room temperature electrical properties data for present samples. It can be observed from the table that the values of d.c.resistivity (ρ) increase with an increase of PbO content.

TABLE II Room temperature data of electrical properties

Sample No.	$\rho \times 10^7$ (Ω-cm)	measured at 1 MHz ε	tanδ	μ_i	(A-m^2/Kg) σ_s
1	4.05	12	0.05	1285	59.5
2	4.41	15	0.05	1144	60.1
3	5.54	15	0.05	1091	61.4
4	12.18	17	0.05	1359	64.2

The increase of ρ in the present samples may be due to formation of PbO as an insulating liquid film on the grain boundaries. A similar result was observed by in the case of conventionally prepared PbO doped MgCuZn ferrites by Rezlescu *et al.* [9]. The present results are compared with those of conventionally prepared samples in Fig. 8.

Table II also give room temperature values of dielectric constant (ε^1), dielectric loss (tanδ) and initial permeability (μ^1) measured at 1 MHz for all the ferrites. It can be seen from the table that an addition of PbO in MgCuZn ferrite led to little increase of initial permeability. The sample with 0.6 wt% PbO has posses

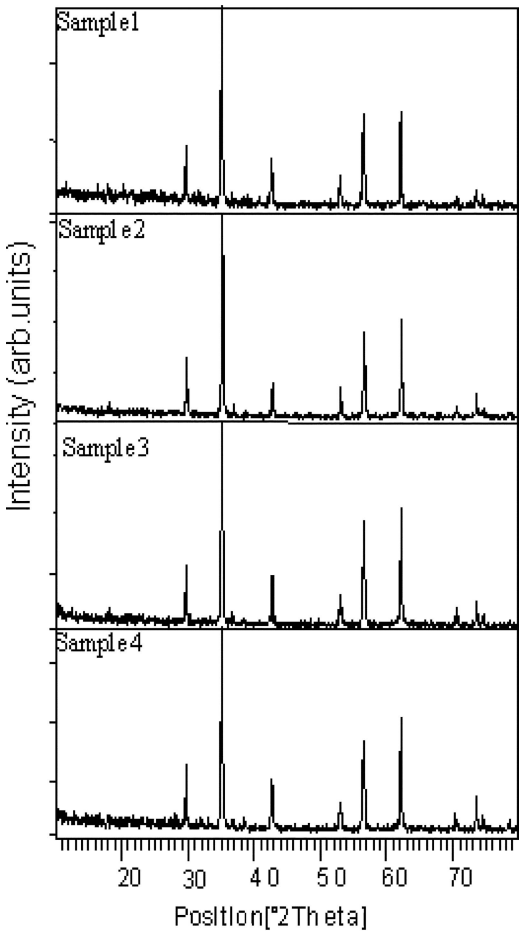

Figure 6 XRD patterns of sintered samples of PbO added MgCuZn ferrites.

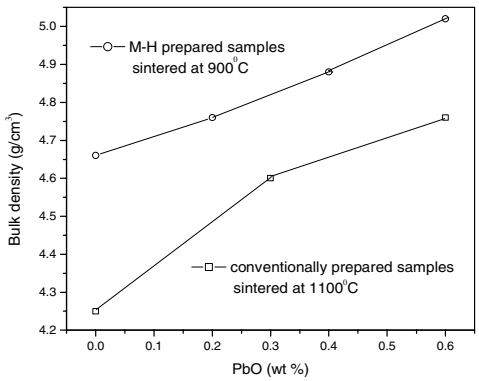

Figure 7 Bulk density graphs of conventional ceramic method and M-H prepared samples of PbO added MgCuZn ferrites.

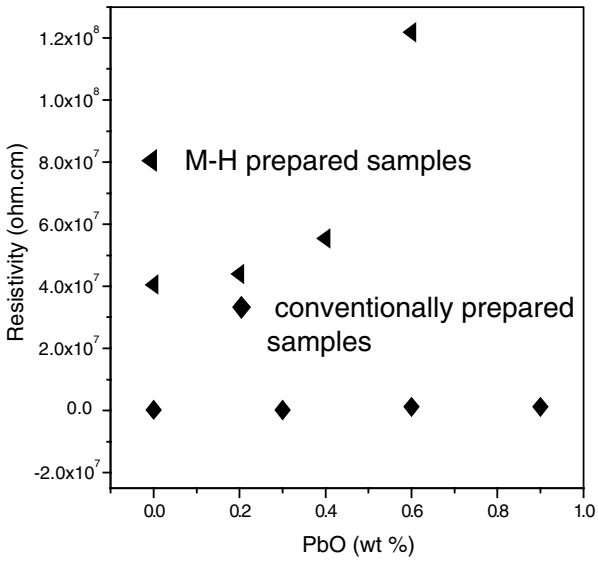

Figure 8 Resistivity graphs of conventional ceramic method and M-H prepared samples of PbO added MgCuZn ferrites.

higher value of initial permeability. The value of dielectric constant slightly increased with an addition of PbO. Dielectric loss for all samples is in the order of 0.05.

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 PbO addition. The increase of the average particle size should be the cause of larger values of the magnetization for the PbO added samples [7, 11].

4. Conclusions

For the first time, nanopowders of PbO added MgCuZn ferrites were synthesized using the microwave-hydrothermal method. Nanopowders were obtained at mild reaction condition and was optimized as 160°C/1 h. The prepared nano powder was characterized using XRD, TEM and IR spectroscopy. In the present investigation MgCuZn ferrite with particles size ∼10–20nm were obtained.

The particle size of the sintered samples is found to be higher than that nanoferrite powder. The properties such as bulk density, resistivity, permeability and saturation magnetization are found to be higher for MgCuZn ferrite with PbO 0.6wt %.

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