Material Science Research India Vol. **5**(1), 125-130 (2008)

Preparation and magneto-electric studies of Nickel Cobalt Manganese Iron oxide (NCMF) and Lead Zirconium Titanate (PZT) nano composites

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(Received: February 19, 2008; Accepted: April 05, 2008)

ABSTRACT

Nickel cobalt manganese iron oxide (NCMF) is a good piezo magnetic material and lead zirconium titanate (PZT) is a good ferro electric material. The composites prepared from NCMF and PZT materials show good magneto –electric effect. In the present work, nano particles of NCMF (crysallites size ~. 13.5 nm) were synthesized by hydrolysis process and PZT (17nm) were obtained by soild state reaction methods . Magnetic behavior of NCMF and electrical behavior of PZT materials were also studied .Resistivity of the materials was measured and magneto electrical study of the composites was made .Magneto –electric composite of piezo magnetic (60% NCMF) and ferro electric (40% PZT) were prepared. On the application of magnetic field , piezo magnetic phase undergoes strain , which applies stress on ferro electric phase and as a result of this voltage is developed across the sample. It was observed that magneto electric effect produced by the composites prepared from nano particles was lower than that of produced from composites prepared from commercially available(coarse size) samples.

Key words: Composite materials; electrical properties; magnetic properties; nanostructures.

INTRODUCTION

Nanosized materials are those which have particles-organic, inorganic or combinations that are of nanometer size (i.e., 10^{-9} m) . These particles can be amorphous, semicrystalline or crystalline . They exhibit many interesting properties and are being increasingly used for new and innovative applications. Composites prepared from nanoparticles can exhibit improved wear resistance, chemical inertness, corrosion resistance and thermal insulating properties[1-2].

A large number of experiments in the recent years have been directed towards measuring the absorption and emission characteristic of single semi conductor nano crystallites. These suggest that the spectra display the characteristics as expected by simple scaling laws[3]. Thus nano crystals may be thought of a new class of tunable dimolecules. Nano meter-sized crystals display clear changes in both the thermodynamic and kinetics of phase transitions, and there is a strong possibility that phases which are unstable are unobserved in the extended solids but may be prepared as nano crystals[4-5]. The smaller the crystal, the lower the melting temperature , and the reduction in the melting temperature is proportional to its surface to volume ratio or inversely proportional to the nano crystal radius. This scaling law of melting temperatures has been seen in many nano crystals. The nanometer-sized ferromagnets are special and because of their smaller size, they behave as single magnetic domains[6-7]. In analogy to single magnetic domains, nano crystals may behave as single structured domains[8-10]. When sufficiently small,on an average, a given nano crystal may contain defects (w.r.t magnetic nano crystals containing only one domain). A defect free crystal will naturally tend to persist in high energy state much longer than on containing defects[5]. It is a remarkable fact that in addition to the profound changes in physical properties the chemical behavior is profoundly altered as well .When an inorganic solid is composed of only a few thousand atoms, it has a large surface area and it is possible to make nano crystals behave chemically just like organic macromolecules.

Nano particles with distinctly different and vastly superior properties have found applications in various fields of industrial and academic interest like semiconductor and electronic industry, catalysis, pharmaceutical industry, coating industry, material science and crystallography[11].

EXPERIMENTAL

Nano particles of $NiFe_2O_4$ have been synthesized by hydrolysis process

5.689g of Ni $(NO_3)_2.6H_2O$ (Merck), 0.1164g of $Co(NO_3)_2$ $6H_2O$,0.1004g of $Mn(NO_3)_2$ 4H2O and 15.352g of $Fe(NO_3)_3.9H_2O$ (MERCK) are dissolved in deionized water(18 M¿) stirred well for 30 minutes and slowly hydrolysed by using NH3 solution till the pH is around 8.0 and brown color precipitate was obtained. This solution was further diluted and stirred well to avoid the agglomeration of the particles. This solution was aged overnight and washed well to remove all unreacted compounds. The wet cake was dried at 80^o C overnight in an oven and powdered manually , using pestle and mortar to get fine powder.

By using citrate process, the above solutions of nitrates are converted into citrates by addition of citric acid. This was dried on a water bath and then left in the oven at 80^o C overnight . The mixture swelled . The dried mixture was crushed and powdered before calcination.

Hydrothermal process

The solutions of Ni $(NO_3)_2$ and $Fe(NO_3)_3$ were taken in an autoclave and was processed for ten hours at 200^o C and 16 kgs/cm^2. A solution was obtained and it was filtered and restored as before. The powder obtained from the hydrothermal process is in the crystalline form and the powders obtained from both hydrolysis and citrate processes is in amorphous form, which need further calcinations for 2 hours at 600^o C to convert into crystalline form. Finally 5.4246 g of $Ni_{0.98}$ $Co_{0.02}$ $Mn_{0.02}$ $Fe_{1.9}$ O_4 (NCMF) was obtained. The PZT powder was obtained by solid state reaction method which involves grinding the PZT material by using mortar and pestle for 8-10 hours in order to make its particle size comparable to that of NCMF.
The composites were electrically poled by applying electric field of 16 kv/cm in a bath of silicone oil for 15 minutes at room temperature and were also magnetically poled at 5 kOe for 30 minutes and magneto-electric studies were carried out by varying AC magnetic field and maintaining DC field. To study the magnetic behavior of the prepared nano ferrites , a torroid was prepared by using the synthesized NCMF and placed in the
B-H measuring set up.

RESULTS AND DISCUSSIONS

The thermogravimetric analysis (TGA) as shown in Fig. 1 , which gives weight loss of the compound by subjecting it to varying temperatures (100-1000° C) shows that there is a loss of physical absorbed water between 100-150°C. The continuous curve between 200-650 °C denotes the crystallization of the material .

The differential thermal analysis(DTA) curve as shown in Fig. 1 shows one endothermic peak between 100-150°C which may be attributed

Table 1: Comparison of magneto-electric properties of nano particles of 60% NCMF and 40% PZT materials with that of the procured materials

S. no.	Particle size (nm)	Sintering for 3hrs (Temp °C)	Resistivity (Ohm-cm)	Electrical poling (kV.cm)	Magnetic poling (kOe)	dE/dH (mV/cm/Oe)
1.	37.0	1150	$3x10^{10}$	20.0	5	16.7
2.	13.5	1150	$1x10^{8}$	16.3	5	4.0

to the evaporation of the physically absorbed water. The endothermic peak at 400°C may be attributed due to the decomposition of hydroxide to oxide.

The XRD graph (Fig. 2) shows no peaks at room temperature of the prepared ferrites and on calcination at 300°C shows peaks and the peaks further intensify (sharp peaks) on calcinations at 600°C matching with those reported (XRD graphs) in the literature.The crystallite size of the prepared NCMF and PZT materials were calculated by using the Sherrer formula . The crystal size of NCMF was 13.59nm and that of PZT material 17 nm.Thus confirming that they are nano size materials.The Scanning electron micrograph of the synthesized particles further confirms that they are of nano size (Fig. 3 -4).

The B-H behavior of the NCMF samples (Fig. 5) shows no hysterisis loop and no coercivity , responding almost linear at room temperature whereas the B-H behavior in Fig. 6 of the commercially obtained NCMF sample shows an hysterisis loop.

The resistivity as given in Table 1 , shows that the resistivity of the prepared sample decreased by two

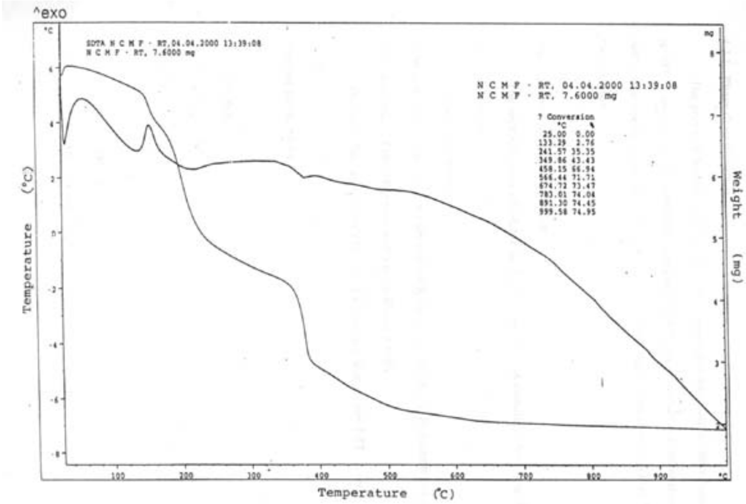

Fig. 1: DTA and TGA curves of NCMF prepared sample

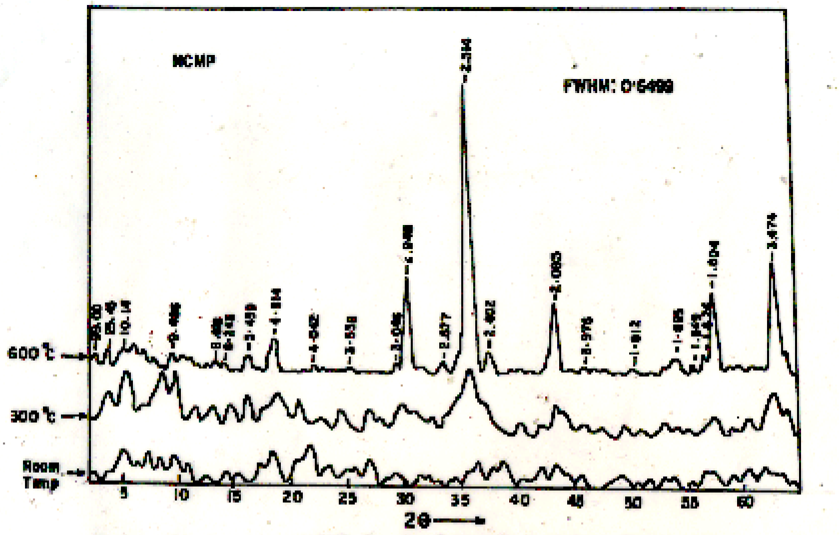

Fig. 2: XRD curves of NCMF samples subjected to various temperatures

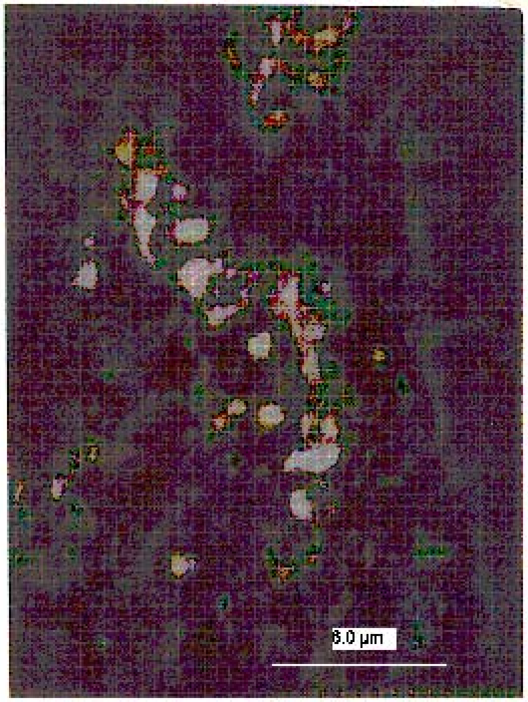

Fig. 3: SEM image of NCMF nano size particles

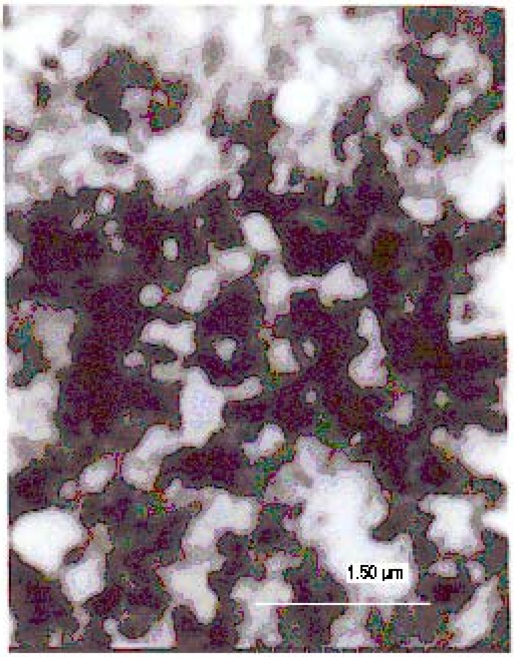

Fig. 4: SEM image of PZT nano size particles

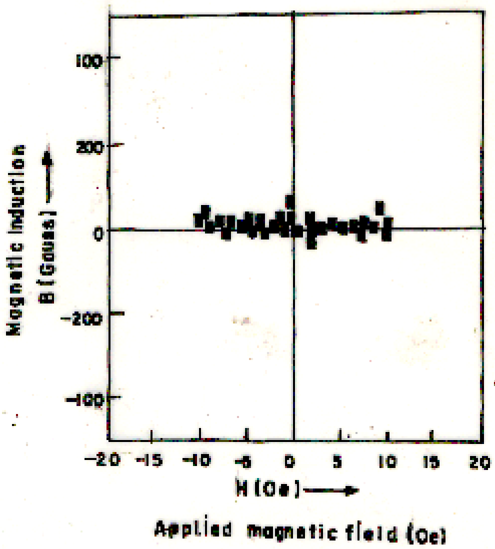

Fig. 5: -H behavior of prepared NCMF samples

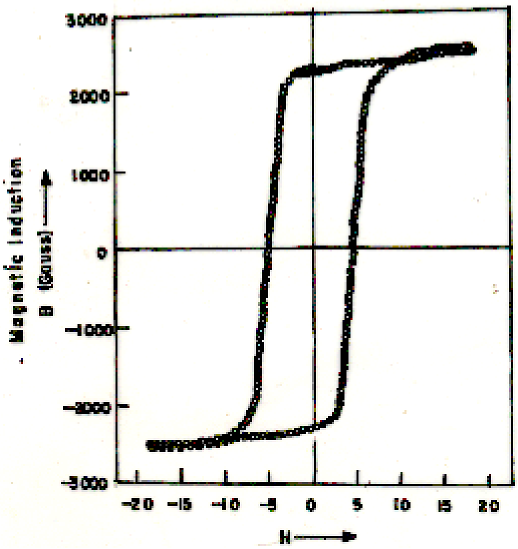

Fig. 6 :B-H behavior of the commercially obtained NCMF sample

orders compared to that of coarse size particles. The more free surface electrons of the nano particles contribute to the reduction in the resistivity of the prepared ferrites. Higher order of resistivity of the ferrites is desired because the sample retains more developed polarization in the materials.

The magneto-electric behavior as given in Fig. 7 and 8 , indicates the prepared nano composites gave lower electric output than that of the coarse size particles for an applied magnetic field. As the composite shows the lower resistivity, the developed polarization discharges into the atmosphere and gives a lower electric output.

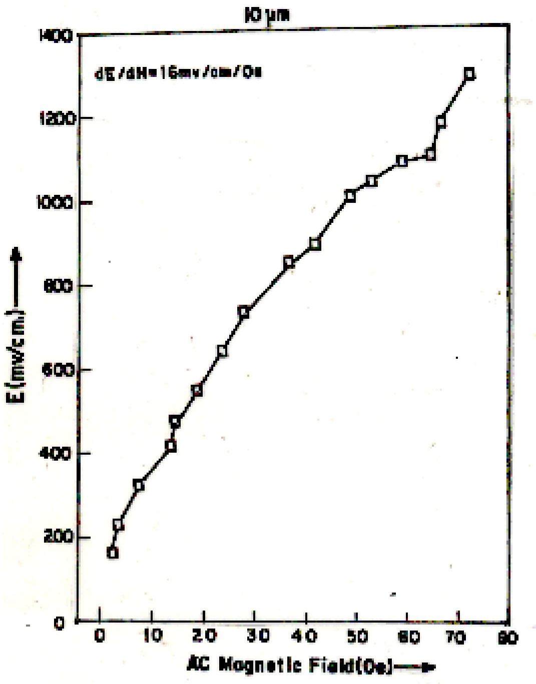

Fig. 7: The magneto- electric curve of prepared nanocomposite (60%NCMF and 40%PZT)

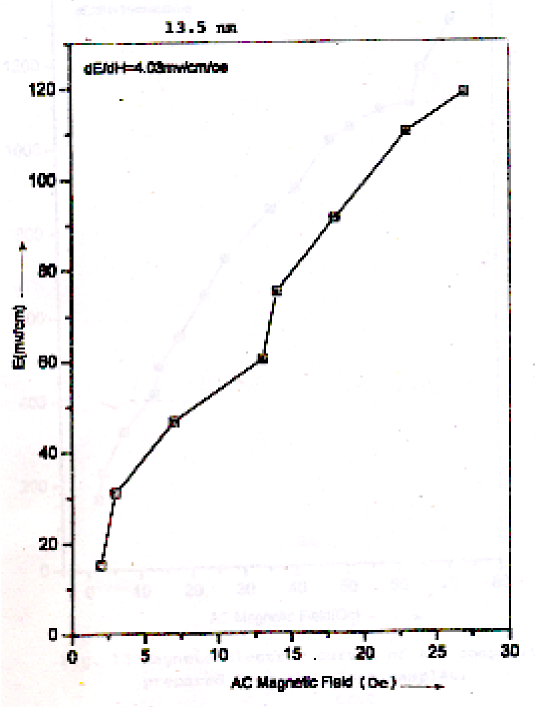

Fig. 8. Magneto-electric curve of the composite prepared from the commercially obtained samples

To probe the characteristics of the nanoparticles, one more magneto-electric composite of lithium-ferrites and PZT materials was prepared where resistivity of the sample decreased much lower than that of the NCMF and PZT composite. As the resistivity of the sample decreased further studies were not carried out. The composite must have higher resistivity so that it can retain more , the developed electrical output.

CONCLUSIONS

Nano crystalline Nickel Cobalt Manganese Ferrites (NCMF) and Lead Zirconium Titanate (PZT) materials were successfully prepared. The samples characterized by using DTA/TGA, XRD and SEM confirms the particle prepared were in the nanometer range (NCMF – 13.5nm and PZT- 17 nm).The magnetic behavior of NCMF sample studied observed distorted magnetic behavior.

The resistivity of NCMF sample (prepared) decreased by two orders compared to the obtained NCMF sample. Magneto-electric studies carried out on the 60 % NCMF and 40% PZT composites (prepared from nano particles) indicated that the magneto-electric output was much more lower compared to that of the composites prepared from the commercially available (coarse size) samples.

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