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Dielectric Studies Of Manganese Carbonate Nanocrystals

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Abstract

Over the past few years, the synthesis and characterization of nanocrystals of materials have become an area of intense research activity. $MnCO_3$ (Manganese Carbonate) is a well known semi conducting material and is highly useful in electronic and optical devices. In the present study, we have made an attempt to prepare $MnCO_3$ (with two different ratios of preparation) with simple domestic microwave assisted solvothermal method. The samples were characterized by TGA analysis. The particle size determination was done using the XRD pattern. The dielectric studies were carried out. The present study indicates that the polarization mechanism in the nano crystals considered is mainly contributed by the space charge polarization. It can be understood that the space charge contribution plays in important role in the charge transport process and polarizability in all the systems considered in the present study.

Keywords: Manganese corbonate, solvothermal method, dielectric measurements

I. Introduction

Over the last few years, the synthesis and characterization of nanocrystals of materials have become an area of intense research activity [1, 2]. Several methods have been reported for the preparation of nanocrystal. $MnCO_3$ (Manganese Carbonate) is a well known semi conducting material and is highly useful in electronic and optical devices. The manganese corbonate nanoparticles can be used as a template for efficient formation of uniform, smooth multilayer polyelectrolyte microcapsules, which are promising systems for biomedical and other applications such as biosensors, bioreactors and drug – delivery devices. The $MnCO_3$ nanocrystals have been prepared by several methods and have been characterized before.Li-Xia Yang have synthesized highly oriented $MnCO_3$ nanocrystal assemblies with an ellipsoidal morphology by ultrasonic solution approach[3]. He Hu et al have synthesized $MnCO_3$ with hierarchical superstructures such as chrysanthemum, straw-bundle, dumbbell and sphere like in water/ethanol system under environment friendly hydrothermal condition[4]. A facile complex homogeneous precipitation method was successfully employed by Shuijin Lei et al for the preparation of $MnCO_3$ and $Mn(OH)_2$ crystals using hydrazine hydrate as the complexing agent in a hydrothermal system[5]. In the present study, we have made an attempt to prepare $MnCO_3$ with two different ratios of precursors by the simple microwave assisted solvothermal method using a somestic microwave oven [6]. The grain sizes of the samples were determined by using the X-ray powder diffraction data. The AC electrical measurements were carried out.

II. Experimental details

The analytical reagent grade manganese chloride and urea with ethylene glycol as solvent were taken as precursors for the preparation of manganese carbonate nanopowders. The required amount of substance (A) was estimated by using the formula,

$$A = \frac{M \times X \times V}{1000} \text{ (in gram units)}$$

Where M is the molecular weight of the substance, X is the concentration in molar units and V is the required volume of solution.

$MnCO_3$ nanopowders were prepared for two molecular ratios of the reactants (precursors). One was mixing manganese chloride and urea in the ratio 1:1 labeled as $MnCO_3$ (1:1) and the next one was mixing manganese chloride and urea in the ratio 1:3 labeled as $MnCO_3$ (1:3). The substances were mixed and dissolved in 200 ml solvent (ethylene glycol) taken in a bowl and kept in a domestic microwave oven. The solution was treated in the microwave oven for about 40 minutes and a colloidal precipitate was formed. The product was cooled naturally at room temperature, then washed with distilled water several times and dried in atmospheric air. The brown precipitate thus formed was again washed with acetone to remove any further impurities present. Thus the pure $MnCO_3$ nanopowders were prepared. The colour of the nanopowders produced was noted. The yield percentage for all the samples were calculated by the formula,

$$\text{Yield percentage} = \frac{\text{Total product mass}}{\text{Total reactants mass}} \times 100 .$$

Using an automated X-ray powder diffractometer (PANalytical) with monochromated CuK_α radiation (λ = 1.54056Å) the powder X-Ray diffraction (PXRD) data were collected for the 2 samples. Using the Scherer formula [7] the grain sizes were determined. The prepared nanocrystals were palletized using a hydraulic press (with a pressure of about 5 tons) and used for the AC

electrical measurements. The flat surfaces of the cylindrical pellets were coated with good quality graphite to obtain a good conductive surface layer. Using a traveling microscope the dimensions of the pellets were measured.

The capacitance (C_c) and the dielectric loss factor (tan δ) were measured using the conventional parallel plate capacitor method using an LCR meter (Agilent 4284A) for the 2 samples with a fixed frequency of 1 kHz at various temperatures ranging from 40 - 150°C. The observations were made while cooling the sample. The temperature was controlled to an accuracy of ± 1°C. Air capacitance (C_a) was also measured for the thickness equal to that of the pellet. The area of the pellet in contact with the electrode is same as that of the electrode. The air capacitance was measured only at room temperature because the variation of air capacitance with temperature was found to be negligible.

The dielectric constant of the pellet sample was calculated using the relation,

$$\varepsilon_r = C_c / C_a.$$

The AC electrical conductivity (σ_{ac}) was calculated using the relation,

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan \delta.$$

Here, ε_0 is the permittivity of free space (8.85×10^{-12} C^2 N^{-1} m^{-2}) and ω is the angular frequency ($\omega = 2\pi f$, where f is the frequency).

III. Results and discussion

Figure 1 shows the photograph of the samples prepared and Figure 2 shows the corresponding pellets .The preparation time, colour and the yield percentage are given in Table 1. The colour of $MnCO_3$ (1:1) nanocrystals observed is dark brown and that $MnCO_3$ (1:3) is light brown. The yield percentage is also significantly high. The results obtained indicate that the solvothermal method is a considerable one for the preparation of $MnCO_3$ nanocrystals.

Table 1: Colour, yield percentage, preparation time and observed average grain size

Sample	Colour	Yield percentage [%)]	Time taken for preparation [min]	Observed average grain size [nm]
$MnCO_3$ (1:1)	Dark brown	4.348	45	29
$MnCO_3$ (1:3)	Light brown	10.219	40	20

Fig. 1 :Powder samples produced: From the left $MnCO_3$ (1:1) and $MnCO_3$ (1:3)

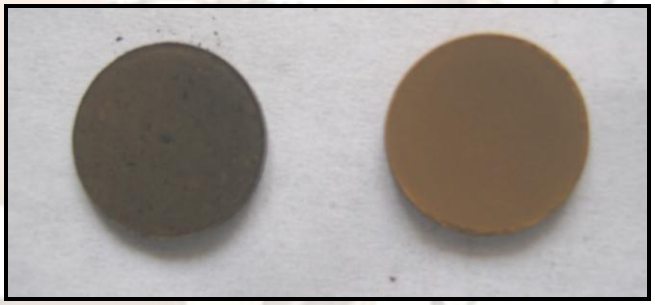

Fig.2 :Pellets of the samples: From the left $MnCO_3$ (1:1) and $MnCO_3$ (1:3)

The PXRD patterns obtained in the present study are shown in Figure 3. The patterns indicate that the samples prepared are of nanostructured. The average grain sizes are also provided in Table 1.

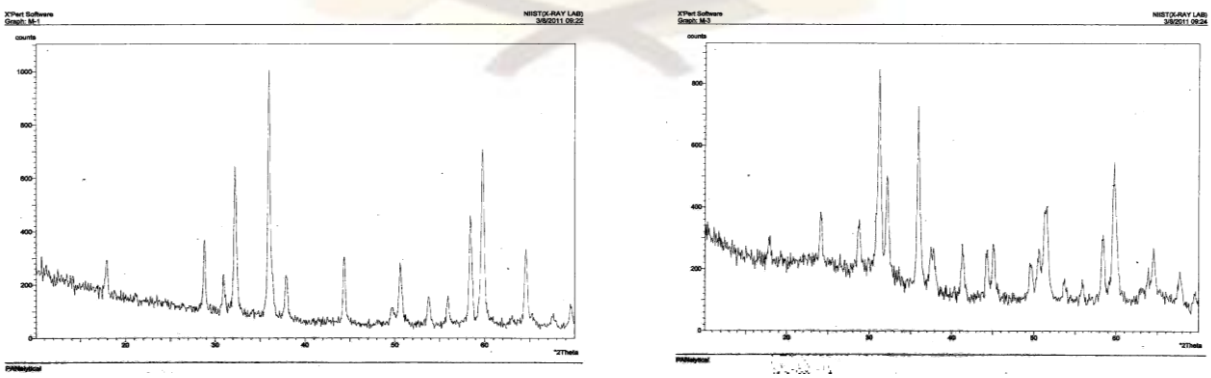

Fig.3: XRD pattern for $MnCO_3$ (1:1) **and** $MnCO_3$ (1:3)

The dielectric parameters viz. ε_r, tan δ and σ_{ac} observed are shown in Figures 4-6. All the parameters increase with increase in temperature.The results obtained in the present study indicate that $MnCO_3$ (1:3) has greater dieleelctric constant than $MnCO_3$ (1:1). The ε_r observed in the present study (at 40°C with a frequency 1kHz) is about 1.05 for $MnCO_3$ (1:1) and 2.4 for $MnCO_3$ (1:3) which is very small when compared to that of the bulk crystal. The dielectric constant is attributed to four types of polarization which are space charge, dipolar, ionic and electronic [8]. At lower frequencies at which all four types of polarizations contribute, the rapid increase in dielectric constant is mainly due to space charge and dielectric polarizations, which are strongly temperature dependent[8,9]. In the case of space charge polarization which is due to the accumulation of charges at the grain boundary, an increase in polarization results as more and more charges accumulate at the grain boundary with the increase in temperature. Beyond a certain temperature, the charges acquire adequate thermal energy to overcome the resistive barrier at the grain boundary and conduction takes place resulting in decreasing of polarization. This interfacial polarization occurs up to frequencies of around 1 kHz with possibly some contribution from the dipolar polarization also as the temperature increases. The grain size observed for the two systems considered in the present study are less than 30 nm. So it can be understood that the polarization mechanism is mainly contributed by the space charge polarization.

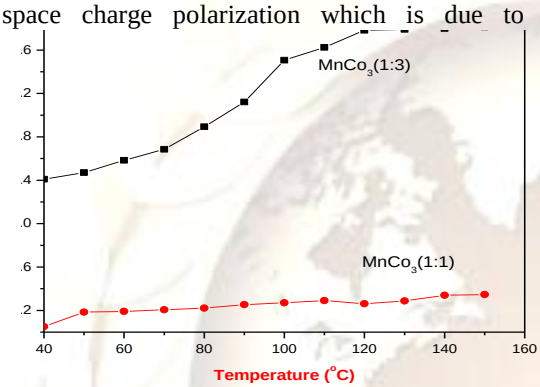

Fig.4: The dielectric constants

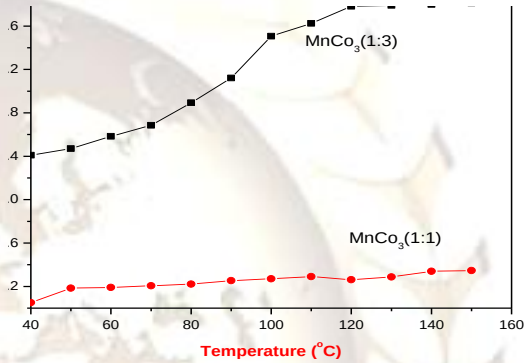

Fig.5: The dielectric loss factors

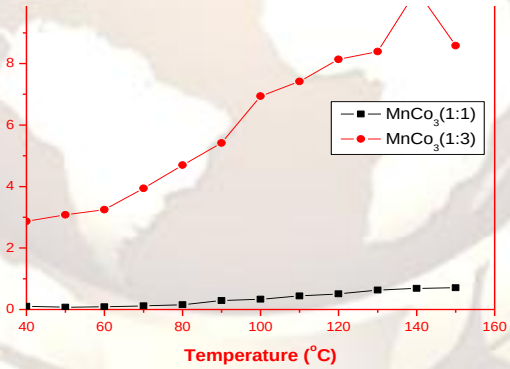

Fig 6; The AC electrical conductivities

Nanoparticles lie between the infinite solid state and molecules. The electrical resistivity of nanocrystalline material is higher than that of both conventional coarse grained polycrystalline materials alloys. The magnitude of electrical resistivity and hence the conductivity in composites can be changed by altering the size of the electrically conducting component. The σ_{ac} values observed in the present study are very small. When the grain size is smaller than the electron mean free path, grain boundary scattering dominates and hence electrical resistivity is increased. Thus the space charge contribution plays an important role in the charge transport process and polarizability in the case of all the systems considered in the present study.

IV. Conclusion

$MnCO_3$ (1:1) and $MnCO_3$ (1:3) were prepared by the simple solvothermal method using a domestic microwave oven and characterized by PXRD and dielectric measurements. The yield percentage and the grain size observed indicate that the method adopted for synthesis of the material is best suited for the preparation of $MnCO_3$

nanocrystals. The dielectric parameters increase with increase in temperature. The results obtained indicate that the space charge contribution plays an important role in the charge transport process and polarizability.

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