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Immense Magnetodielectric Effect in Eu_2O_3-Mesoporous Silica Nanocomposites

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Nanodimentional Eu_2O_3 was developed inside the channels of silica with mesoporus structure, which have5 nm pore diameter. At room temperature, such nanocomposite showed a large magnetodielectric coefficient of around 70% upon application of magnetic field of 1 Tesla at a frequency 1 kHz. The dielectric loss was quite low in spite of the fact that Eu_2O_3 is conducting in nature. This was achieved because of a scarcely dispensed Eu_2O_3species inside silica, which is highly resistive in nature. This method of nanocomposite formation gives rise to the fabrication of devices with high magnetodielectric coefficients.

Keywords: Nanocomposites; Mesoporous silica; Magnetodielectric effect

1 Introduction

Due to their wide implementations for practical[1-3], multiferroic materials are of immense importance. Presence of two or more ferroic phases in a composite material produces a large magnetoelectric coupling in comparison to that or a single phase multiferroic system[4, 5]. Nanocompositemultiferroics with different morphologies *e.g.* multilayers, nanotubes, nanoparticles, thin film in a matrix have been synthesized and their properties studied[6-8]. A structure or system which posses an interfacaes between two phases with very different electrical conductivities and one of the phases having a magnetoresistance characteristic, exhibits magnetodielectric effect[9].

For the fabrication of materials with mesoporous structure, several types templates or replicas have been employed. These have high surface areas and large pores and hence have extensive potential applications, such as, for sensors technology, energy conversion along with storage for rechargeable battery, magnetic materials, biomedicine as a drug delivery system *etc*[10-16]. Eu_2O_3 has been studied after growing them in different matrices[17,18]. These materials are used in electronic circuits, colored television, optical sensors *etc*[18-21]. The structure of Eu_2O_3 is changed when it is confined within a nanometer sized mesoporous material[22]. Eu_2O_3 nanocrystals dispersed in amorphous Al_2O_3 show strong photoemission[23]. Nanoparticles (NPs) of oxides of rare earth elements grown within Silicon dioxide (SiO_2) glass framework have shown high dielectric permittivity with magnetodielectric effect (MDE)[24]. In this work we have synthesized Eu_2O_3 nanoparticles within mesoporous silica. A large magnetodielectric effect in the Eu_2O_3-mesoporous silica nanocomposite was observed. Detailed discussions are outlined in this article.

2 Experimental Methods

Following the methodologies published previously, KIT-6 (mesoporous silica template of our concern) in powder form was prepared[25]. One gm of P123 was taken as a soft template. It was made solubilized into 36 gm of distilled H_2O and 1.96 gm of concentrated (35%) hydrochloric acid. The mixture was stirred for one hour at the temperature 308 K. After that, One gm of C_4H_9OH (butanol) was added into it, followed by stirring of another one hour and subsequent addition of 2.15 gm of tetraethyl orthosilicate (TEOS).Whole combination was kept on stirring for 24 h at the same temperature condition. Later the mixture was shifted into a teflon-lined autoclave made of stainless steel. It was handled in hydrothermal fashion at 393 K for one day (24 h). Distilled water was used to wash the filtered product. The same was dried for one day at 333 K. This generated white powdered sample. To get rid of the surfactant, it was calcinated for

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5 h at 823 K. Impregnation techniques was used to synthesize the nano-composite. $Eu(NO_3)_3$ (europium nitrate) was dissolved into EtOH (Ethanol). KIT-6 silica powder (0.5 gm) was plunged into that EtOH solution of europium nitrate salt. The mixture was stirred for 24 h. Absorbed KIT-6 was filtered, followed by washing with EtOH and distilled H_2O and was accumulated after drying for one week at room temperature. Final dry powder was sintered for four hours at 873 K.

JEOL 2010 Transmission Electron Microscope (TEM) was used to investigate the morphology of the composite sample. Pellet specimens were generated using cold press of 5 tons load applied into the powder, taken in a mould of one cm diameter. 0.5 mm was the typical thickness of the sample. The pellets applied as electrodes were painted by silver paste on its both surfaces. The silver paste was bought from M/S Acheson Colloiden (Netherland). Samples were held in between the poles of an electromagnet during the study of their magneto-dielectric property. It was provided by M/S Control Systems & Devices, Mumbai. Agilent E4890A precision LCR meter was utilized for measurement of change of capacitance against applied magnetic field.

3 Results and Discussions

Transmission electron micrograph (TEM) of the KIT-6 substrate is depicted in Fig. 1(a). It is visible that the pore channels have widths of about 5 nm. Microstructure of the Eu_2O_3 embedded KIT-6 nanocomposite is shown in Fig. 1(b), which exhibits some portions of the channels is packed with europium oxide. It is supported by electron diffraction data from Fig. 1(b) that is displayed in Fig. 1 (c). From Fig. 1 (c) inter-planar distances were estimated. The results are observed as being in excellent accordance with the data for europium oxide from the JCPDS (File No. 76-0154). It's indeed clear that mesoporous silica's pores have a sparse distribution of the europium oxide phase. EDAX analysis of the nanocomposite shows the existence of a component consisting europium in the nanocompositeshows in Fig. 2. The other components present being silicon and oxygen.

Inside a Quantachrome Autosorb-1 C around 77 K, we performed nitrogen (N_2) adsorption/desorption experiments to verify the existence of Eu_2O_3 inside the pore channels of mesoporous silica. Based on the findings, we estimate that around16.8% of the volume of the nanochannels contain Eu_2O_3 phase. The findings were encapsulated in the Table 1.

It is evident from the transmission electron micrograph of the prepared nanocomposite, that the material would function like a Maxwell-Wagner dielectric [26] in the presence of an ac electric field. It is a consequence of the fact that Eu_2O_3 [~ 10^{-6} $ohm^{-1}cm^{-1}$] phase and silica phases' [~ 10^{-18} $ohm^{-1}cm^{-1}$] have huge difference in their electrical conductivity values [27]. Fig. 3(a) and (b) illustrate the fluctuation of the real component ε' and imaginary component ε'' of the dielectric permittivity of the nanocomposite system respectively, with frequency under various temperature values. According to the kind of variation curves, it was evident that the space charge polarization exhibits a dielectric dispersion[26].

The change of the real part of dielectric constant ε' as a function of the magnetic field recorded for the frequencies of 1 and 100 kHz at room temperature is

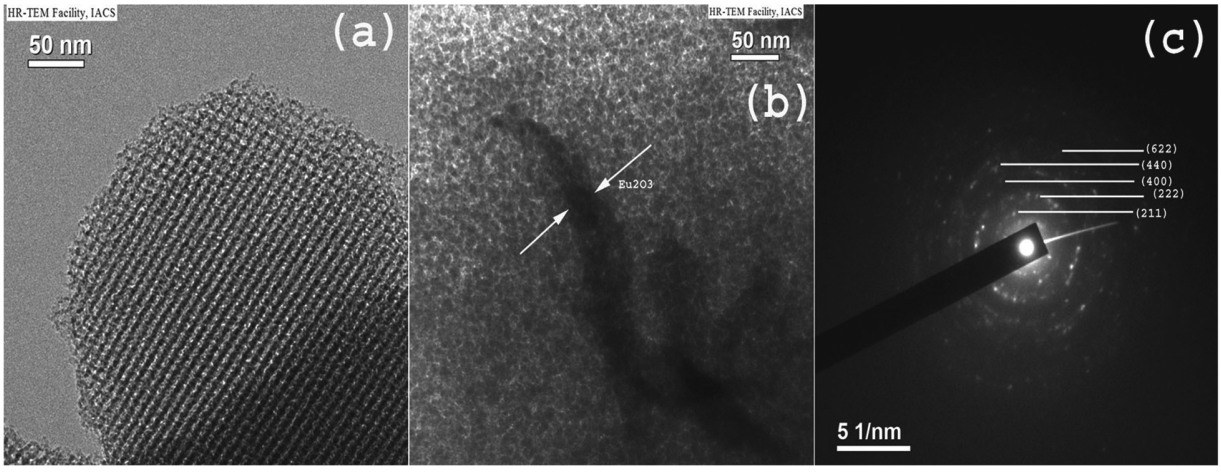

Fig. 1 — (a) Transmission Electron Micrograph of the KIT-6 mesoporous silica template. (b) Transmission Electron Micrograph of the nanocomposite. (c) Electron Diffraction Pattern of figure (b).

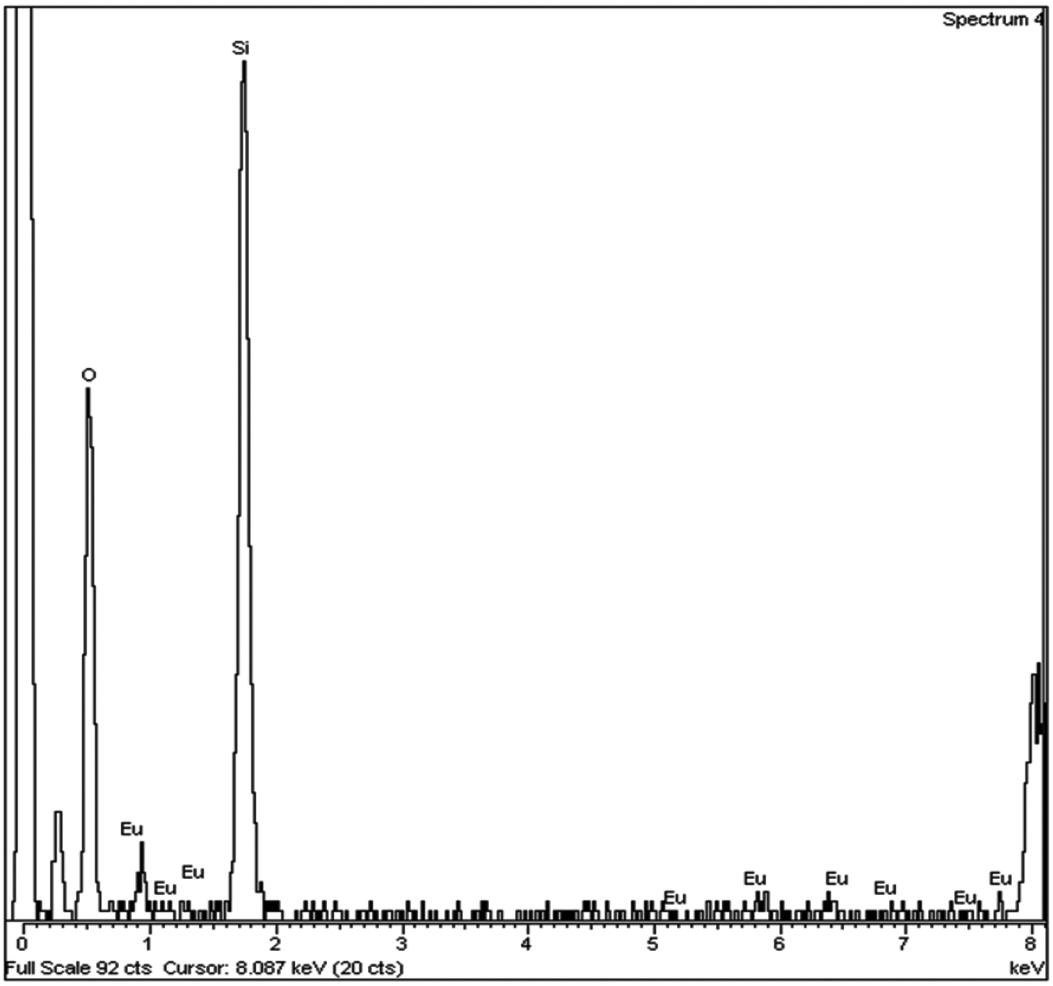

Fig. 2 — EDAX analysis of nanocomposites.

Table 1 — Value of BET surface area and Specific pore volume from N_2 adsorption/desorption measurements

Specimen	BET surface area (m^2g^{-1})	Specific pore volume (cm^3gm^{-1})
KIT-6	617	0.9725
Eu_2O_3- KIT-6	302	0.8090

shown in Fig. 4(a) and (b) respectively. It is clear that the dielectric constant rises as the applied magnetic field was increased. Magneto-dielectric coefficient (M.D.) value which is outlined by M.D. $= \frac{\varepsilon(H)-\varepsilon(0)}{\varepsilon(0)}$ is calculated at different frequencies for 1 Tesla magnetic field. Table 2 displays the encapsulated results. It was found that for 1 kHz the value of MD% was 70% which is very high indeed. As a variable of magnetic field, the dielectric constant's imaginary portion, ε'', decreases. Magneto-dielectric loss ($\tan\delta = \varepsilon''/\varepsilon'$) should be obvious to be in the span of 0.085 to 0.056 which is shown in Fig. 5 for the frequency of 10 kHz. Typical results were obtained for other frequencies also. The values of magneto-dielectric loss for different frequencies are summarized in Table 2. The maximum value of magneto-dielectric loss for frequency 1 kHz was around 0.1. Therefore the nanocomposite with large MD effect and low magneto-dielectric loss will work perfect as magnetic sensors in smart various devices.

Our analysis of the magneto-capacitance nature is based on a heterogeneous system composed of two components, silica and europium oxide, with interfaces among them and significantly unlike electrical conductivities. Such a system's impedance could be expressed as the series combination of two capacitors having various dielectric loss coefficients. It was established from the pertinent equation that the effective dielectric constant ε' is determined by[9]

$$\epsilon'(\omega) = \frac{1}{C_0(R_i+R_b)} \frac{\tau_i+\tau_b-\tau+\omega^2\tau_i\tau_b\tau}{1+\omega^2\tau^2} \quad \ldots(1)$$

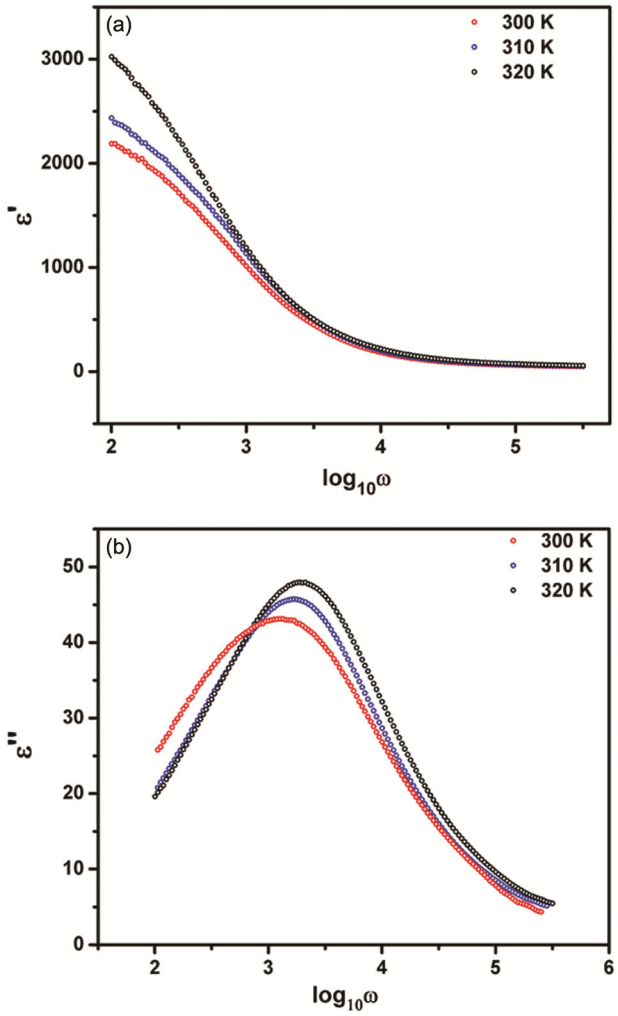

Fig. 3 — Variation of the (a) real part of permittivity ($\mathcal{E}'$) and (b) imaginary part of permittivity ($\mathcal{E}''$) for the nanocomposite as a function of frequency measured at different temperatures.

R_b= resistance of europium oxide phase, R_i= resistance of the interfacial layer generated by silica, $\tau_i = C_i R_i$,C_i= capacitance of the mesoporous silica phase; $\tau_b = C_b R_b$, C_b= capacitance of the europium oxide layer; $\tau = (\tau_i R_b + \tau_b R_i)/(R_i + R_b)$ and$C_0 = \epsilon_0 A/t$, A = surface area of the specimen capacitance, t = thickness and $\mathcal{E}_0$= free space dielectric permittivity. Experimental data could be fitted into

Table 2 — Value of MD% and range of magneto-dielectric for different frequencies

Frequency in kHz	Value of MD% for 1Tesla	Range of magneto-dielectric loss (tanδ)
1	74	0.074-0.105
10	43	0.056-0.085
50	33	0.043-0.061
100	26	0.033-0.047

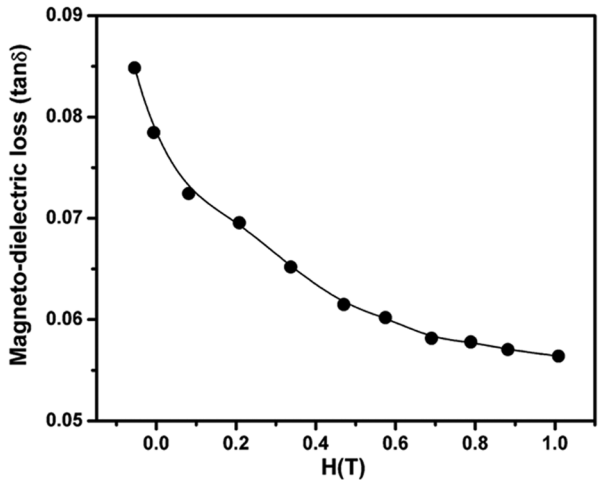

Fig. 5 — Variation of magneto-dielectric loss (tanδ) as a function of magnetic field at room temperature measured at a frequency 10 kHz

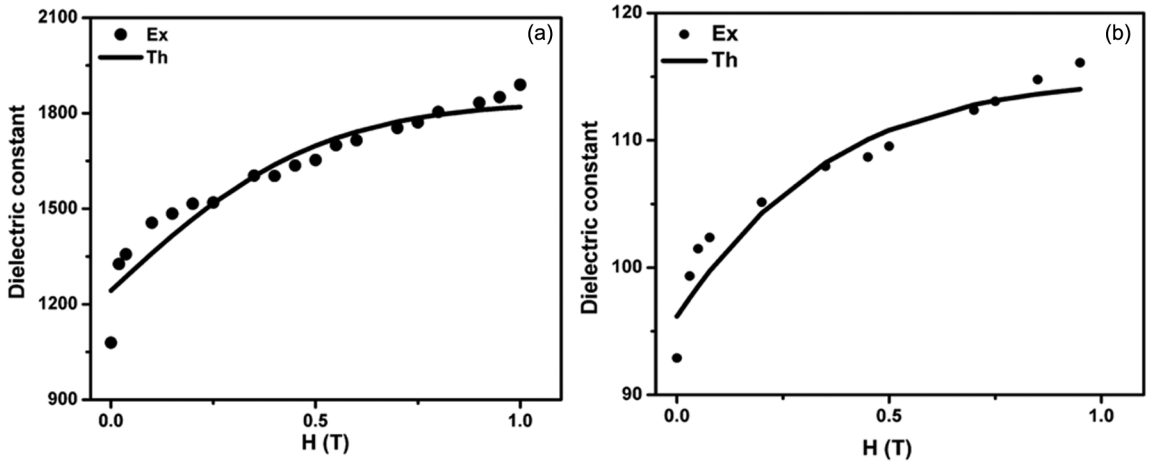

Fig. 4 — Variation of real part of permittivity ($\mathcal{E}'$) as a function of magnetic field at room temperature measured at a frequency (a) 1 kHz and (b) 100 kHz.

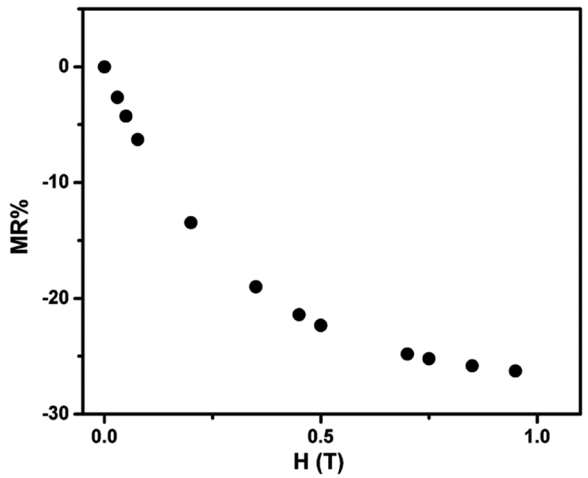

Fig. 6 — The variation extracted value of magnetoresistance with magnetic field at 100 kHz.

equation (1), just by considering magnetoresistance of the nanosized europium oxide layer have negative values with the configuration given in equation 2.

$$R(H) = R_0 + R_1 \exp\left(-\frac{H}{H_S}\right) \quad \ldots (2)$$

Where, R_0, R_1 and H_S are being the fitting constants. In Fig. 4(a) and (b), the solid line represents the theoretically fitted curve. It is evident that the theoretical findings and the experimental facts agree satisfactorily. Fig. 6 illustrates the manner of extracted magnetoresistance change in the nanophase of europium oxide for the frequency of 100 kHz. Such results were obtained for other frequencies also. For an applied magnetic field of one Tesla, it's indeed clear that this phase exhibits a resistance drop of roughly 29%.The magnetoresistance of europium oxide has never been documented to have decreased by such a significant amount. We attribute such phenomenon to the europium oxide's nanoscale size.

It may be pointed out that some recent measurements on composites consisting of Eu_2O_3 nanoparticles dispersed in a silica glass matrix exhibit magnetodielectric effect with the dielectric constant decreasing depending on the magnetic field that is being used[28]. Similar kinds of outcomes were also found for nickel zinc ferrite nanoparticles dispersed in a silica system [29]. In the present work, however, a positive value of magnetodielectric coefficient was observed. We ascribe this difference to the mechanism responsible for the magnetoresistance in the two systems. Spin-polarized electron tunneling between the magnetic particles has been proposed as the cause of magnetoresistance. This should be easier in the case of a composite with vacuum in between the magnetic particles.

4 Conclusions

In conclusion, the nanochannels of mesoporous silica KIT-6 with a channel diameter of approximately 5 nm were used to develop the europium oxide component. The real and imaginary components of the dielectric permittivity displayed dispersal as a function of frequency, which is feature of a Maxwell-Wagner capacitor. At room temperature, the composite system demonstrated a significant magneto-dielectric coefficient of 70% upon application of magnetic field of one Tesla with frequency of one kHz. Despite the fact that europium oxide being typically thought to be a poor insulator, the system's dielectric loss was rather low due to the phase's scant distribution inside the pores of silica matrix which is highly resistive. This method of composite synthesis will enable the production of materials with high magnetodielectric coefficient values for use in devices.

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