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Dielectric and Magnetic Characterization of Sol-Gel Synthesized $SrMnO_3$ Perovskite

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ABSTRACT

Large exchange coupling has been reported in B-site magnetic perovskites which results in higher magnetic ordering temperatures. $SrMnO_3$ is a perovskite manganite which has strong magnetostructural and magnetoelectronic effects such as colossal magnetoresistance, thus making it feasible in applications like magnetic sensors and information storage. Here we report a phase pure synthesis of $SrMnO_3$ using sol-gel auto-combustion method. The crystal structure was optimized by sintering the prepared samples at temperatures like 400 °C, 600 °C, 800 °C, 1000 °C and 1200 °C for 4 hours. Structural studies through X-ray diffraction confirms the formation of perovskite $SrMnO_3$. Dielectric studies were performed through impedance analyzer revealed the semiconducting behavior as the sintering temperature is raised. The magnetic study through vibrating sample magnetometer discloses enhancement of magnetization due to the ion displacement effect when the sintering temperature was changed.

1. Introduction

Perovskites are the family of composite materials having a structure type ABX_3, related to the structure of $CaTiO_3$. $CaTiO_3$ is a mineral discovered by Gustav Rose in 1839 and discussed its structure. He observed that the structure of $CaTiO_3$ is based on primitive cubic unit cell and thus they are named separately as Perovskites [1-3]. In a single unit cell of the perovskite compound, eight A cations occupy the corners, while B cation occupies the body-center position. The B cation is surrounded by an octahedron of anions in which the oxygen anions are most stable. Since then many perovskites of the ABX_3 type have been discovered and their structure varies from orthorhombic to cubic and hexagonal perovskites. These structure variations exists due to the tolerance factor which depends upon the size of the A atom. The tolerance factor is given by:

$$t = \frac{r_A + r_0}{\sqrt{2}(r_B + r_0)} \quad (1)$$

Where r_A and r_B are the ionic radii of A and B atoms respectively. For cubic perovskite to be formed t should in the range 0.9-1. If tolerance factor is higher than 1 hexagonal perovskites are form and if the value of *t* is less than 0.9 then orthorhombic perovskites are formed.

$SrMnO_3$ is a rare type of a compound which shows a polymorph between hexagonal and cubic perovskites [4, 5]. This is because the ionic radius of Sr lies in between smaller Ca and larger Ba ions of the group 2A in the periodic table. Due to this unique behavior $SrMnO_3$ shows some pronouncing behaviors like magneto-structural and magneto-electronic effects which make it feasible to be used in transducers and information storage. In particular, $SrMnO_3$ have been fabricated to explore its properties and applications to be used as a catalytic agent for the combustion of hydrocarbons because of its microstructure. This property arose because microstructures have high surface area and are of nanosized particles which is the basic requirement of good ceramic catalyst [6]. Paramagnetic to ferromagnetic transition have been reported earlier for $SrMnO_3$. These transitions occur mainly due to the increase of doping concentration in A atom site which is Sr [7]. Sakai et al. reported its electronic properties and mentioned $SrMnO_3$ as a mott insulator with a conductivity value lies in the range of 6×10^{-6} S cm^{-1} which was observed by using a DC four probe method [8]. Some exciting results showing antiferromagnetic behavior with 278 K as Neel temperature was obtained Stolen et al [9].

In this study we present the fabrication of $SrMnO_3$ compound through sol-gel auto combustion route. The dielectric properties and magnetic properties were investigated at room temperature.These studies proposed that preparation technique, annealing temperatures and structural morphology directly influenced the various magnetic and electrical properties.

2. Experimental

In order to fabricate the $SrMnO_3$ compound we dissolved the analytical grade salts of Strontium nitrate

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$[Sr(NO_3)_2.\ 6H_2O]$ and Manganese Nitrate $[Mn(NO_3)_2.\ 6H_2O]$ in deionized water with a molar ratio of 1:2 with metal nitrates to citric acid. All salts and acids were purchased from Sigma Aldrich (USA) having more than 99% purity. The solution was then constantly stirred and a temperature of 150 °C was maintained using a Hotplate and Magnetic stirrer. After sometime xerogel was formed which was then converted into powder by self-combustion at a temperature of 300 °C. This burnt powder was than sintered at 400, 600, 800, 1000 and 1200 °C to make five different samples starting from a, b, c, d, and e respectively. After sintering, the powder was compressed into pellets using a hydraulic press having a diameter of 10 mm and thickness of 1.5 mm. The dielectric and impedance analysis were performed using a Precision Impedance Analyzer. The magnetic studies were performed using a Lake Shore 7407 Vibrating Sample Magnetometer.

2. Results and Discussion

3.1 Dielectric Studies

The dielectric constant of the pellets of sintered samples was measured by using the relation [10, 11]:

$$\mathcal{E}' = \frac{AC}{\varepsilon_0 d} \qquad (2)$$

Where A is the surface area of the pellet, C is the capacitance, $\mathcal{E}_0$ is the vacuum permittivity and d is the thickness of the pellets. Fig. 1 shows the variation of dielectric constant ($\mathcal{E}'$) with frequency on the x-axis. The dielectric properties were studied on a wide range of frequency from 20 Hz to 20 MHz (which was then converted into the logarithmic scale ranges from 1.3 - 7) separately for five different samples. In the Fig. 1 it can easily be seen that all the samples show an increasing behavior when the frequency is decreased. At lower frequency the value of dielectric constant is high while at higher frequency the value of dielectric constant is low.

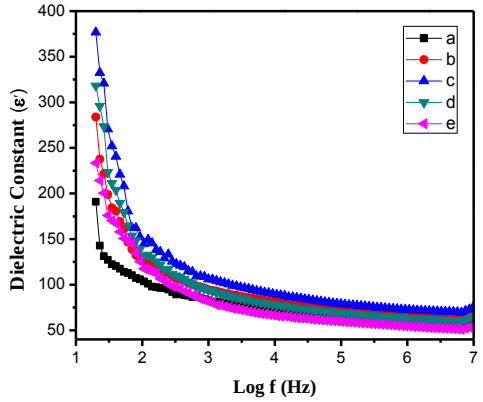

Fig. 1: Dielectric Constant behavior for all the samples

The reason for this behavior is explained in terms of interfacial polarization as explained by Maxwell-Wagner effect [12]. This effect explains the polarization effect by considering the solid-pore-solid interfaces covered with opposite charges. When the frequency is low the charges could easily transfer their position. But when the frequency becomes too high, charges do not find time to re-assemble themselves they becomes distorted. Thus only at lower frequencies our samples shows the dielectric behavior.

Sufficiently high dielectric value of the sample c (blue line) is obtained which shows that ionic displacement can cause difference in dielectric values. B cations changes their position due to the different sintering temperatures and thus can introduce different properties [8, 13].

Fig. 2 shows the graph of complex part of the dielectric with the frequency. It could be seen that the graphs shows the decreasing behavior as the frequency increases and comes to a point of saturation at high frequency. Secondly, the value of complex dielectric constant decreases as we move towards the samples with higher sintering temperature.

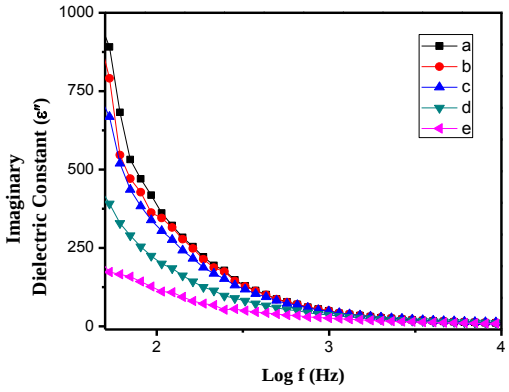

Fig. 2: Imaginary dielectric constant behavior for all the samples

Fig. 3 shows the collective behavior of dielectric constant and imaginary part of the dielectric constant in the form of the Cole-Cole graph. The Cole-Cole graph is obtained from the complex analysis of the dielectric properties which are obtained from the Debye relations which represents the complex dielectric constant in terms of the real and imaginary part.

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \qquad (3)$$

$$\varepsilon' = \varepsilon_s + \frac{\varepsilon_s - \varepsilon_\infty}{1+\omega^2\tau^2} \qquad (4)$$

$$\varepsilon'' = (\varepsilon_s - \varepsilon_\infty) + \frac{\omega\tau}{1+\omega^2\tau^2} \qquad (5)$$

$\mathcal{E}_s$ is the permittivity at constant electric field and $\mathcal{E}_\infty$ is the permittivity at highest frequency which is mainly lies on the origin. The decreasing behavior of dielectric constant graph can also be explained in terms of these equations in which it is clearly shown that frequency is inversely proportional to dielectric constant. In Fig. 3 the plot

shows the curves of ε^*. The curve of the first sample is an incomplete semi-circle which means that our first sample is a fairly good dielectric material but after that poorly resolved semicircles can be seen in rest of the samples which predicts some losses and thus the dielectric behavior is decreased [14].

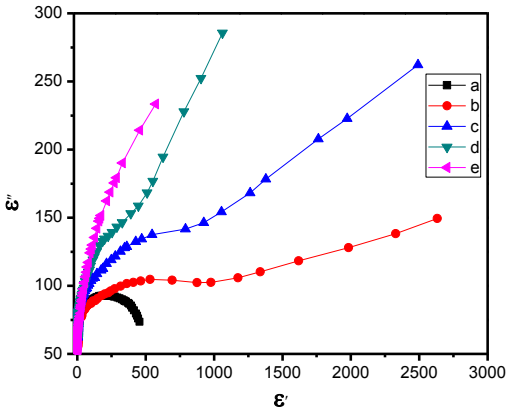

Fig. 3: Cole-cole plot

3.2. *Magnetic Response Studies*

Fig. 4 describes the magnetic field response of the material through the MH-loop which was obtained through a vibrating sample magnetometer. The maximum magnetic field applied to the samples is 10 kOe. All the measurements were carried out at room temperature. The parameters measured form this techniques are saturation magnetization (M_s), coercivity (H_c) and retentivity (M_r). All the results are summarized in Table 1.

Fig. 4 reveals that very little hysteresis is obtained for all the samples but the maximum coercive field (H_c) is obtained for the sample sintered at 800 °C and 1200 °C. The remanence (M_r) and saturation magnetization (M_s) of these samples are also maximum. The saturation magnetization of all the samples is reached at nearly same magnetic field which is 9500 Oe approximately. This shows that the magnetizing and de-magnetizing power of all the samples remains same even at elevated sintering temperatures [15].

Low values of retentivity and coercivity depicts the anti-ferromagnetic behavior of the $SrMnO_3$ as the susceptibility of the antiferromagnetic materials is very low usually in the range of 10^{-2} cm/g. Thus the area of the hysteresis loop is very small for the antiferromagnetic materials [16].

Table 1: Magnetic parameters

Sintering Temperatures (°C)	400	600	800	1000	1200
M_s (emu/g)	0.12	0.102	0.121	0.114	9.89
H_c (Oe)	97.3	112.46	453	125	410
M_r(emu/g)	0.002	0.0021	0.009	0.002	0.004

Table 1 clarify the values of the parameters calculate from the MH-loop. Till 800 °C the coercivity increases and then at 1000 °C it decrease and increases again at 1200 °C. This behavior can be explained in terms of the ionic displacement of the manganese ion [8, 13, and 17]. Since the perovskite structure of $SrMnO_3$ is most stable at near 1000 °C the ionic displacement is negligible and thus very small magnetic behavior is observed which initiate very few magnetic ordering in the lattice. As we go towards the lower temperature the distortion in the position of manganese ion increases and we observe the maximum magnetic behavior at 800 °C which depicts the maximum magnetic ordering. Similarly at higher temperature this behavior of the manganese ion is observed.

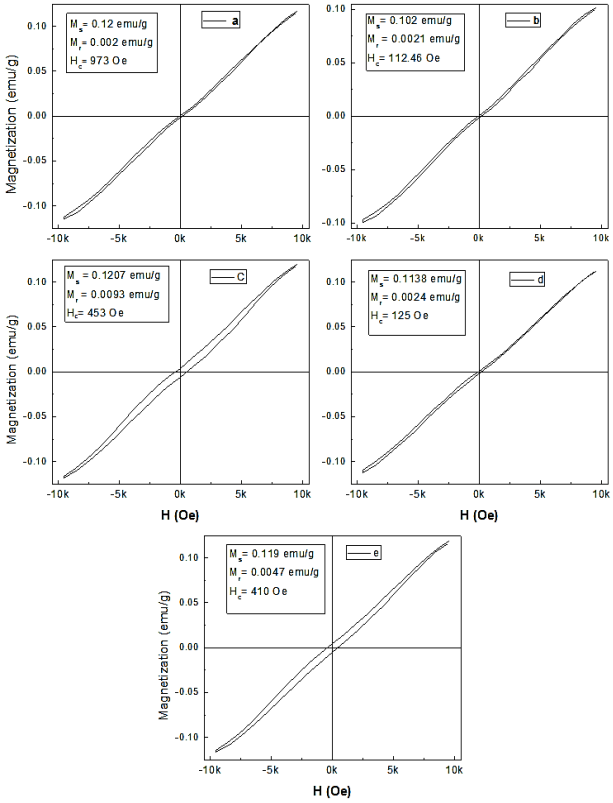

Fig. 4: MH-loops of the SrMnO3 samples sintered at (a) 400 °C, (b) 600°c, (c) 800 °C, (d) 1000°C and (e) 1200°C

4. Conclusion

$SrMnO_3$ sample was fabricated through sol-gel auto combustion route after setting the metal nitrate and citric acid ratio as 1:2. After the combustion a burnt powder is obtained which was grinded and was placed in an oven for sintering at different temperatures which makes our sample as (a) 400 °C, (b) 600°C, (c) 800 °C, (d) 1000 °C and (e) 1200 °C. The dielectric and magnetic studies were performed by using an Impedance Analyzer and a vibrating sample magnetometer. These properties were studied as a function of the sintering temperature. The

dielectric studies reveal the Maxwell-Wagner polarization effect in which the value of dielectric constant decreases with the increase in frequency. The Cole-Cole graph shows the decrease in dielectric behavior as the sintering temperature is increased showing semiconducting behavior. The magnetic study reveals the dependence of ionic displacement of the manganese ion on the magnetic behavior of $SrMnO_3$. The saturation magnetization is maximum for sample (c) and (e) which reveals the highest magnetic ordering.

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