The Effect Of Metallic Inclusion On The Capacitance Of Fe_3O_4 As Dielectric Matrix

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Abstract

We observe a large drop in capacitance when small volume fraction of copper as metallic fillers is embedded into Fe_3O_4 dielectric matrix system. On further inclusion, a jump in capacitance is observed above percolation threshold which is not in accord with the conventional percolation phenomenon. To understand the nature of this dielectric response we have also measured the dc conductivity of our composite system Fe_3O_4:Cu at room temperature corresponding to different range of metallic volume fraction. A power law behavior near threshold yields a non-universal value of critical exponent which is mainly attributed to tunneling effect in disordered system.

Keywords: Capacitance, critical exponents, dielectric, percolation, conductivity.

1. Introduction

The composite systems have recently gained a huge attention in developing multi- functional sensors, energy storage devices, biocompatible polymers and various semiconductor based composite devices [1–5]. Geometrical phase transition is one of the interesting phenomena in composite systems where interconnectivity of one component in presence of other leads to a rich physical phenomenon called percolation. It is a common phenomenon in a composite system (metal-insulator) where connectivity among small finite metallic clusters leads to formation of one infinite cluster that spans the entire system. This also results in a power law behavior of many electrical and geometrical parameters at threshold. As for example, near the percolation threshold the resistance (R) of a composite system follows as $R \sim |\Phi - \Phi_c|^{-t}$, where Φ is a volume fraction and t is the critical exponent[6]. The behavior of classical random disordered system near percolation threshold has been an interesting subject for many scientific investigators since long period of time. In particular large enhancement of dielectric permittivity and dc conductivity by 3-5ordersofmagnitudehigherisobservedatpercolation threshold in various metal-dielectric and metal-insulator composite systems [7,8]. This has opened up a new opportunity for the development of embedded capacitor technology and in spintronics.

Achieving large volumetric capacitance based on sharp increase of dielectric permittivity near percolation threshold was originally proposed by Efros [9,10]. Moreover the additional advantage of this technique is the charging and discharging time which is found to be significantly smaller than the conventional capacitor or batteries.

In our paper, we have studied the percolation behavior in dielectric-metal composite system which is represented as Fe_3O_4:Cu. Here, we have shown a non-monotonic variation of percolative capacity of Fe_3O_4 as a dielectric matrix upon limited in- corporation of Copper (Cu) as metallic filler. The magnetite Fe_3O_4 is a magnetic semiconductor known to have versatile physical properties depending on their crystal structure and composition. On the other hand, copper is considered to be good electrical conductor at room temperature. Unlike conventional percolative composites we have found a sharp drop in capacitance at small volume fraction of Cu followed by a small jump in capacitance above percolation threshold. In addition, to anticipate the growth of metallic clusters within the matrix, we have also performed measurement of dc conductivity. We found a sharp change in resistance near the threshold which agrees well with the classical percolation. But far above the threshold another increase in resistance is also observed along with the jump in capacitance as found from dielectric spectroscopy.

2. Experimental details

Commercially available Fe_3O_4 and Cu nano-particles were brought from sigma aldrich of high purity. To make a composite system, cu particles of increasing volume fraction were mixed with the Fe_3O_4 and was thoroughly mixed until the color of the resultant powder looks uniform. Volume fraction (Φ) is given as the ratio of volume fraction of copper and the total volume of each composites. After mixing they were compressed using 20 Ton KBR pellet press machine at room temperature. The resulting pallet was then examined by x-ray diffractometer for the verification of the crystal structure and other impurity phase. FTIR was also performed to trace any moisture in our composite system. Four-point contact technique is used to determine dc conductivity on each of the composites of varying metallic fraction. A LCR meter of oscillating frequency range 100Hz to 25KHz under 1V peak to peak ac signal is used for dielectric spectroscopy.

3. Results and discussions

3.1 Measurement of dc resistance on composites

Fig.1 shows X-ray diffraction of a Fe_3O_4:Cu composite system at room temperature. It confirms the absence of any major impurity in as prepared sample.Fig.2 shows the behavior of dc resistance for increasing volume fraction(Φ) of copper in Fe_3O_4 matrix system. At $\Phi = 0$ i.e. for pure Fe_3O_4 the resistance is around 5.2KΩ. On increasing the volume fraction of Cu till 0.048, the slope of the resistance curve of the composite system is much steeper. For $\Phi > 0.048$ the drop in magnitude appears slower respect to former region.

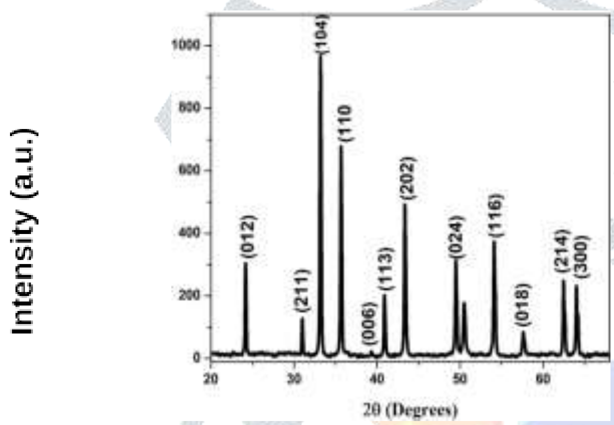

Figure1: XRD pattern of Fe_3O_4:Cu composite system. No other impurity peak is found in the system.

This particular volume fraction at which two different slopes of the curve coincides is known as percolation threshold (Φ_c). Physically this implies that at this particular value of volume fraction the first infinite cluster of copper fillers is formed which spans the entire dielectric matrix.

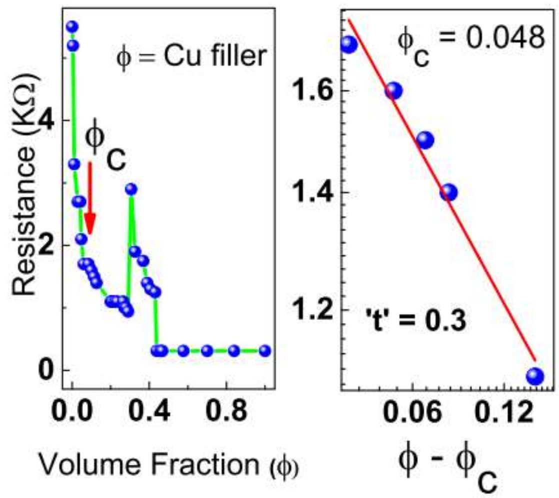

Figure 2: Left side: Variation of dc resistance as a function of metallic volume fraction. Above percolation threshold steep rise in resistance is observed. Right side: power law behavior with critical exponent 0.3 is observed at the threshold.

This also suggests that for $\Phi < \Phi_c$ the current through the composite system is mainly due to flow of charge carriers through Fe_3O_4. Whereas for $\Phi > \Phi_c$ the current chooses the percolating cluster of lowest resistance (Cu path) whose thickness also increases on addition of more cu fillers. Now for $0.3<\Phi<0.45$ a significant change in resistance behavior is again Observed which does not agree well with the percolation theory. This led us to belief that some other physical phenomenons like localization of charge carriers may have restrict

The flow of current [11, 12]. This charge localization is a result of space charge effect between two Cu clusters separated by Fe_3O_4 dielectric component. To shed more light into this effect we have also performed dielectric study of these same pellets of composite systems. The right-hand side panel of Fig. 2 shows a log-log plot which represents the power law behavior at the vicinity of percolation threshold. At threshold the resistance of a metal-insulator composite system is expected to diverge with critical exponent t = 2 which is considered to be universal [13, 14]. But in our case Fe_3O_4 is not a good insulator and supports a finite conductivity. This makes our composite system metal- dielectric due to which our exponent t is found to be around 0.3 which is much lower than the universal value. This low value of exponent t can be attributed to tunneling effects between finite and infinite metallic clusters. Earlier non universal values of critical exponents are also observed and reported in other composite systems [15].

3.2 ***Dielectric measurement of the composites***

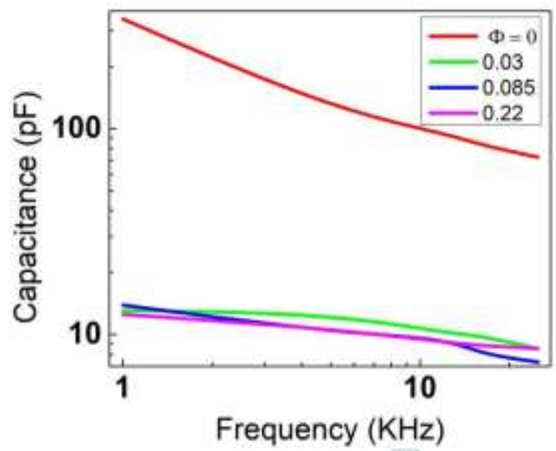

Figure3: Capacitance as a function of ac frequency for different values of metallic volume fraction. Large difference in capacitance on small fraction of metallic inclusion is observed.

Fig.3 represents a logarithmic plot of the capacitance as function of oscillating frequency of the input ac field. The absence of capacitance plateau at low frequency implies presence of conducting grains that enhances the leakage current in all the composites.

The origin of this conducting grains is mainly from the dielectric matrix Fe_3O_4. It is also found that on incorporating small volume fraction of Cu(Φ>0.03) in the matrix there is a sharp drop in capacitance. Although the dc characteristics represents the percolation behavior, the ac response does not have a conventional percolation type behavior.

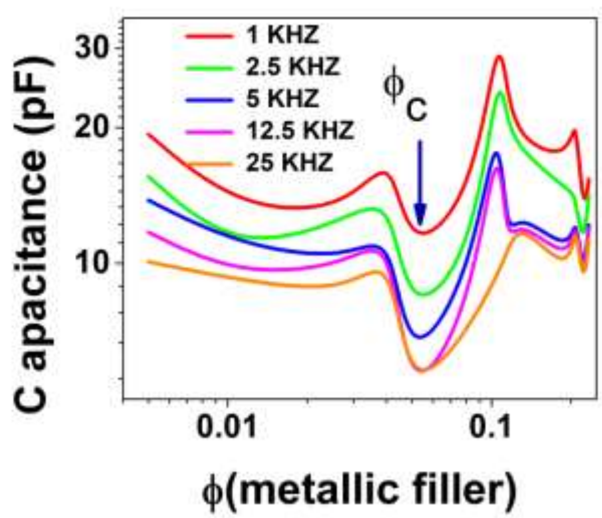

Figure 4: Capacitance as a function of metallic volume fraction for specific values of input ac frequency. A dip followed by small jump in capacitance above percolation threshold is observed.

Small fraction of copper particles has proved to be enough to increase the conductivity of charge carriers which in turn enhances the loss or the imaginary part of dielectric permittivity. Consequently, this reduces the real part of the dielectric permittivity or the capacitance by factor of 15. All other composites with varying metallic volume fraction are found to have similar dielectric response.

Fig. 4 shows the dependence of capacitance at various range of frequencies as a function of Φ in Fe_3O_4 composite system. Series of composites show a dip in capacitance at percolation threshold Φ_c followed by a jump in capacitance at relatively higher volume fraction. This drop in capacitance at threshold in our composite is in contrast with the classical percolation phenomenon where large enhancement of dielectric constant or capacitance is observed. This dip in capacitance can be due to tunneling of charge carriers between finite metallic clusters [16]. This further supports the idea of tunneling effect which is also observed in dc measurement. Moreover, the jump in capacitance at higher volume fraction ($\Phi > \Phi_c$) is mainly due to space charge effect which makes the charge immobile. Further increase of Φ results in merging among many metallic clusters due to which the barrier or the charge localization weakens and capacitance again drops. In future, temperature dependent study would help us to understand the tunneling effect in more better way.

4. Conclusion

In conclusion, we have fabricated Fe_3O_4:Cu composite system by incorporating metallic cu at different volume fraction in dielectric Fe_3O_4 matrix. On addition of Cu, the onset of percolation begins at low volume fraction. Below Φ_c sharp upturn of resistance in the composite system is observed. Around threshold, tunneling effect dominates which results in a lower value of critical exponent. Moreover the

dielectric measurement performed on Fe_3O_4:Cu system also yields an unconventional percolation behavior. Both space charge effect and tunneling effect are attributed to this non-universal behavior.

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