EVALUATION OF MAGNETIC AND DIELECTRIC STUDIES OF Cu DOPED TiO₂ NANOPARTICLES

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Abstract - This paper puts forward the contribution of Cu ions on the dielectric feature and magnetic properties of titania nanoparticles with stoichiometric formula Ti1-xCuxO₂ (x = 0.00, 0.03, 0.05 and 0.07). The frequency dependent dielectric properties at room temperature have been investigated using LCU meter. Field and temperature dependent magnetic measurements have been done using VSM and SQUID magnetometers. The presence of AFM coupling has also been analyzed quantitatively. Enhancement in the dielectric property in Cu doped TiO₂ NPs is an additional advantage for the viewpoint of device application in nano-sized dielectric materials. This AFM coupling along with superexchange interaction reduce the magnetic moment of the Cu doped TiO₂ NPs and weak ferromagnetism is observed in the synthesized Cu doped TiO₂ samples.

Keywords - TiO₂ nanoparticles, VSM, AFM and SQUID.

I. INTRODUCTION

One of the magnificent approaches to create novel functional materials for achieving rich functionality is to consolidate different physical properties into one. Understanding the physics behind these novel properties of pure and doped transition metal oxides (TMOs) semiconductor represents a major challenge in fundamental and applied research today. There is a growing interest in nanoscaled semiconductors due to their impact in catalytic, electrical, optical, and magnetic applications [1]. Major research efforts have recently been placed on the fabrication and characterization of nano-sized dielectric materials, because the current technology requires very small size particles to miniaturize microwave devices and components. Recently, TiO₂ (titania) has attracted attention for its use in fabricating capacitors in microware devices due to its high dielectric constant.

Nano titania is a cost effective material which also has the advantages of unusual high dielectric constant [2, 3], promising chemical stability [4] and thermal stability [5, 6] It is expected to replace traditional capacitor dielectrics and dielectric resonators. Titania exists in three polymorphs: anatase, rutile and brookite. The majority of dielectric applications are affected by the presence of these Cuystalline polymorphs, morphologies, cations distribution and doping by ions [7]. At small particle sizes, the anatase is more stable than the rutile structure [6].

The focused interest on high dielectric constant materials is driven by the need to fabricate more reliable high capacitance DRAM cell and hence to achieve high density DRAMs. Although TiO₂ possesses the advantages of high dielectric constant (ε₉ ~ 60 to 100) [3, 4] but enhancement in the property is an additional profit for the viewpoint of device application.

Since the discovery of room temperature (RT) ferromagnetism in anatase Co doped TiO₂ [8], there has been much focus on such system [9-12] as a DMS to provide efficient injection of spin-polarized carriers for semiconductor spintronic devices.

II. MATERIALS AND METHOD

Chromium doped TiO₂ NPs with stoichiometric formula Ti₁₋ₓCuxO₂ (x = 0.00, 0.03, 0.05, and 0.07) were prepared by acid modified sol-gel route.
The Cu crystalline and phase of the Cu doped samples were analyzed by XRD. The lattice parameters and other detailed structural information were obtained by using Powder X software followed by the Rietveld refinement. FESEM, HRTEM and EDS investigated at UGC-CSIR Lab in Lucknow. Morphological and elemental details accordingly. Raman analysis was also carried out for further confirmation of single phase. It is found that synthesized undoped and Cu doped TiO₂ NPs are in anatase type tetragonal structure.

Undoped and Cu doped TiO₂ pallets of diameter 12.6 mm and thickness 1.2 mm were prepared and sintered at 450°C for 6 hrs. The pallets were coated with silver paste on opposite faces to form parallel plate capacitors with the synthesized product acting as dielectric medium. Dielectric properties were studied as a function of frequency in the range 85 kHz - 5 MHz using an Agilent LCU meter (4285A). Magnetic hysteresis loops of undoped and Cu doped samples were measured at room temperature using a vibrating sample magnetometer (VSM). Moreover, field dependent specific magnetization (M-H) at 300 K, and temperature dependent magnetization (M-T) measurements were carried out with a superconducting quantum interference device (SQUID) magnetometer.

III. RESULTS AND DISCUSSIONS

The dielectric properties of material are influenced by many factors like method of preparation, structural homogeneity, cations distribution, density, porosity, history of sintering, introduced strain, polarization, doping by ions, etc. There are various quantities, which explain the dielectric properties.

The real part of the complex dielectric constant εα is the high-frequency dielectric constant associated with displacements of ionic charge distributions relative to their nuclei. The lattice contribution, ε₁ arises from displacements of ions and their charge distribution, εd represents a dipolar contribution, through charge carrier hopping. Generally, εα and ε₁ are frequency and temperature independent at relatively low temperatures. This behaviour was observed for the pure as well as Cu doped TiO₂ NPs. Simultaneously, there is an enhancement in the dielectric permittivity with increasing Cu doping concentration.

The dielectric loss (tanδ) in a system is a measure of lag in the polarization with respect to the external applied a.c. field. Dielectric loss tangent (tanδ) is associated to the loss of energy from the applied field into the sample (this energy is dissipated as heat) and therefore it is denoted as dielectric loss. Variation in dielectric loss (tanδ) with frequency for undoped and Cu doped TiO₂ NPs. Since tanδ is directly proportional to the imaginary part of dielectric constant (ε'').

Magnetic Properties

Field Dependent Magnetization by VSM

The magnetic properties of the Cu doped TiO₂ NPs were investigated at room temperature using VSM. They represent the field dependent specific magnetization M-H curves of undoped and Cu doped TiO₂ NPs respectively. Literature reports that the undoped titania is diamagnetic (DM) in nature at the temperature higher than 20 K.

It indicates unavailability of considerable number of oxygen vacancies or defect to impart ferromagnetism after overcoming diamagnetism properly. On the other hand, incorporation of Cu into titian host matrix generates considerable number of defects nearby Cu ions for exchange interaction to occur.

The in plane hysteresis loop of doped sample represents distinct evidence, although response is quite weak, for FM ordering of Cu doped TiO₂ NPs at room temperature. Until now, there is an incomplete understanding on the exact origin of ferromagnetism in oxide based DMS materials and question remains against the origin. Phase analysis strikes out the possibility of Cu clustering or any Cu oxide phase as there is no trace of any secondary phase other than the anatase TiO₂ up to the detection limit of XRD, HRTEM and Raman analysis.
For quantitative evaluation of the intrinsic magnetic coupling between the Cu ions of Ti$_{1-x}$Cu$_x$O$_2$ (x = 0.03, 0.05 and 0.07) NPs, M-T measurements of all the doped samples have also been performed under ZFC condition. The field is higher than the maximum field at which hysteresis loop is observed in M-H curves. The inverse susceptibility with temperature (1/\chi - T) curves exhibit typical antiferromagnetic (AFM) behaviour but they deviate slightly from linearity at lower temperature region. To analyze such type of (1/\chi - T) variations, one can make a linear fit of the high temperature inverse susceptibility data, which follows Curie-Weiss law of the form \chi \theta (where, x is the molar concentration of Cu atoms; C(x) is Curie constant and \theta(x) is the Curie-Weiss temperature. The negative values of Curie-Weiss temperature confirm the presence of AFM coupling in Ti$_{1-x}$Cu$_x$O$_2$ (x = 0.03, 0.05 and 0.07) samples which is gradually inCueasing with Cu concentration. Last two interactions lead to reduction of observed FM ordering..

IV. CONCLUSION

The present investigations also clearly point out that the weak ferromagnetism at room temperature in the Cu doped samples may be caused by the exchange interactions between Cu ions and oxygen vacancy in the titania host lattice. Although, in the high field region, M-H curves do not show any saturation for Cu doped TiO$_2$ NPs. A large amount of paramagnetic (PM) contribution to the M-H data is present. After subtraction the PM component mathematically, the Cu doped samples show ferromagnetic hysteresis loop with saturation magnetization of the order of 10$^{-3}$ emu/g, which increases as the Cu doping concentration increases.

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