PHYSICS   **RESEARCH ARTICLE**

Characterization of dielectric and magnetic studies of Cr doped Tio2 nanoparticles

Venkateshwarlu. Kalsani
Department of Physics, KITS, Warangal, Telangana State, India - 506015.

ABSTRACT

This paper puts forward the contribution of Cr ions on the dielectric feature and magnetic properties of titania nanoparticles with stoichiometric formula $Ti_{1-x}Cr_xO_2$ (x = 0.00, 0.03, 0.05 and 0.07). The frequency dependent dielectric properties at room temperature have been investigated using LCR 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 Cr doped TiO_2 NPs is an additional advantage for the viewpoint of device application in nano-sized dielectric materials. This AFM coupling along with super exchange interaction reduce the magnetic moment of the Cr doped TiO_2 NPs and weak ferromagnetism is observed in the synthesized Cr doped TiO_2 samples.

Keywords: TiO2 nanoparticles, *LCR* meter, VSM, AFM and SQUID.

1. 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]. Amongst many other interesting properties, size dependent properties of semiconductor nanoparticles (NPs) are unique. 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, TiO_2 (titania) has attracted attention for its use in fabricating capacitors in microelectronic 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 crystalline 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 TiO_2 possesses the advantages of high dielectric constant (ε_r ~60 to 100) [3, 4] but enhancement in the property is an additional profit for the view point of device application.

Since the discovery of room temperature (RT) ferromagnetism in anatase Co doped TiO_2 [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. Absence of Co metal clusters in anatase Co doped TiO_2 exhibits ferromagnetic behavior above RT with n-type semiconducting properties [8, 9, 12, and 13]. There are some experimental reports [14, 15] that show the crucial role played by the oxygen vacancies in the formation of a long-range ferromagnetism order in Cr and Co doped TiO_2 systems. The exact origin of ferromagnetism, its

relation to the presence of free carriers and, most important, whether the carriers are spin-polarized in these doped oxides are still under much debate.

2.   MATERIALS AND METHOD

Chromium doped TiO$_2$ NPs with stoichiometric formula Ti$_{1-x}$Cr$_x$O$_2$ (x = 0.00, 0.03, 0.05, and 0.07) were prepared by acid modified sol-gel route.
The crystalline and phase of the Cr 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 Indore. Morphological and elemental details accordingly. Raman analysis was also carried out for further confirmation of single phase. It is found that synthesized undoped and Cr doped TiO$_2$ NPs are in anatase type tetragonal structure having space group **I4$_1$/amd.** Undoped and Cr doped TiO$_2$ pallets of diameter 12.9 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 75 kHz - 5 MHz using an Agilent LCR meter (4285A). Magnetic hysteresis loops of undoped and Cr 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.

3.   RESULTS AND DISCUSSIONS

The dielectric properties of material are influenced by many factors like method of preparation, structural homogeneity, cations distribution, grain size, density, porosity, history of sintering, introduced strain, polarization, doping by ions, etc. There are various quantities, which explain the dielectric properties.
The most instructive presentation of dielectric data is given in terms of frequency dependent dielectric permittivity or dielectric constant (ε^*) defined in equation. Where, ε' and ε'' are the real and imaginary part of the dielectric constant. The real part of the complex dielectric constant can be expressed as $\varepsilon' = \varepsilon_\alpha + \varepsilon_1 + \varepsilon_d$, where ε_α is the high-frequency dielectric constant associated with displacements of ionic charge distributions relative to their nuclei. The lattice contribution, ε_1 arises from displacements of ions and their charge distribution, ε_d represents a dipolar contribution, through charge carrier hopping. Generally, ε_α and ε_1 are frequency and temperature independent at relatively low temperatures. This behaviour was observed for the pure as well as Cr doped TiO$_2$ NPs. Simultaneously, there is an enhancement in the dielectric permittivity with increasing Cr 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 Cr doped TiO$_2$ NPs. Since tanδ is directly proportional to the imaginary part of dielectric constant (ε'').

The dielectric loss increases from lower to higher frequencies until a relaxation peak is observed at mid-frequencies and then it decreases with further increase in frequency. Low frequency region is not represented properly within due to the frequency limitation of the LCR meter. The broad peak observed in mid frequency characterizes the loss spectrum.

A.C. Conductivity
$\sigma(\omega) = A\, \omega^s$ where, A and s are constants that depend upon both the temperature and composition; A has the units of conductivity; s is dimensionless and ω is angular frequency of the applied field. The value of s lies between 0 and 1. When s = 0, the electrical conductivity is frequency independent (d.c. conductivity) and for s ≤ 1, the conductivity is frequency dependent (a.c. conductivity). It shows the variation of a.c. conductivity with frequency for undoped and Cr doped TiO$_2$ NPs at room temperature. Initially, σ_{ac} increases slowly with the increase in frequency but at higher frequency conductivity shows a higher increasing rate. This behaviour of a.c. conductivity can be explained by hopping model. At low frequencies, the conductivity is less and the transport takes place in an infinite paths. However, for the σ_{ac}, the transport is through the hopping

process of the charge carriers. Here, the increase in frequency of the applied field enhances the hopping of charges between the charge carriers Ti^{4+} and Ti^{3+}, which causes an increase in the mobility of carriers and, thereby, increases the σ_{ac}. For Cr doped samples, hopping of charges between Cr^{3+} and Cr^{2+} is additional contribution that dominates charge carriers blocking effect in σ_{ac}. Hence, σ_{ac} increases with the increasing Cr concentration.

Magnetic Properties

Field Dependent Magnetization by VSM

The magnetic properties of the Cr doped TiO_2 NPs were investigated at room temperature using VSM. They represent the field dependent specific magnetization M-H curves of undoped and Cr doped TiO_2 NPs respectively. Literature reports that the undoped titania is diamagnetic (DM) in nature at the temperature higher than 20 K.

There are many reports on ferromagnetism in undoped TiO_2 thin films without any magnetic impurities or magnetic ion doping. Most of them accused to the presence of oxygen vacancies on the surface or interface of the films for this unexpected FM ordering. The very weak FM ordering at low field in the synthesized undoped titania sample may be due to the presence of oxygen vacancy or defect associated with NPs. It indicates unavailability of considerable number of oxygen vacancies or defect to impart ferromagnetism after overcoming diamagnetism properly. On the other hand, incorporation of Cr into titian host matrix generates considerable number of defects nearby Cr 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 Cr doped TiO_2 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. Is it an extrinsic effect due to direct interaction between the local moments in transition metal impurity clusters or indeed an intrinsic property caused by exchange coupling between the spin of the carriers and the local magnetic moments? Phase analysis strikes out the possibility of Cr clustering or any Cr oxide phase as there is no trace of any secondary phase other than the anatase TiO_2 up to the detection limit of XRD, HRTEM and Raman analysis.

For quantitative evaluation of the intrinsic magnetic coupling between the Cr ions of $Ti_{1-x}Cr_xO_2$ (x = 0.03, 0.05 and 0.07) NPs, M-T measurements of all the doped samples have also been performed under ZFC condition at a field strength of 4000 Oe. 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) behavior 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 Cr atoms; C(x) is Curie constant and θ(x) is the Curie-Weiss temperature. The negative values of Curie-Weiss temperature confirm the presence of AFM coupling in $Ti_{1-x}Cr_xO_2$ (x = 0.03, 0.05 and 0.07) samples which is gradually increasing with Cr concentration. Last two interactions lead to reduction of observed FM ordering. Actually, in competition among these spontaneous interactions (i.e. FM, AFM and super exchange), stronger FM interaction dominates and that is, on an average, reflected in M-H measurement. All the experiment results are shown in **Fig.1, 2, 3, 4 and 5**.

4. CONCLUSION

In summary, undoped and Cr doped anatase TiO_2 NPs of basic composition $Ti_{1-x}Cr_xO_2$ (x = 0.00, 0.03, 0.05 and 0.07) were successfully synthesized by simple acid modified sol-gel method. The TiO_2 NPs has high dielectric constant and display a gradual dielectric relaxation in the high frequency region. The incorporation of Cr ions significantly enhances the dielectric constant as well as a.c. conductivity of TiO_2. The loss tangent peaks appearing at a characteristic frequency suggest the presence of relaxing dipoles in all the synthesized samples, whereas, it increases with increasing Cr doping and is gradually shifted towards higher frequency region. The present investigations also clearly point out that the weak ferromagnetism at room temperature in the Cr doped samples may be caused by the exchange interactions between Cr ions and oxygen vacancy in the titania host lattice. Although, in the high field region, M-H curves do not show any saturation for Cr 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 Cr doped samples

show ferromagnetic hysteresis loop with saturation magnetization of the order of 10^{-3} emu/g, which increases as the Cr doping concentration increases.
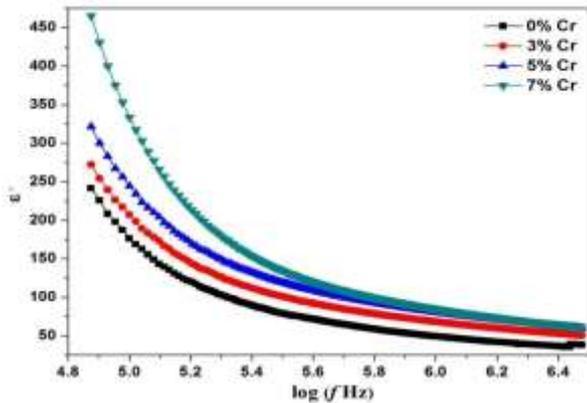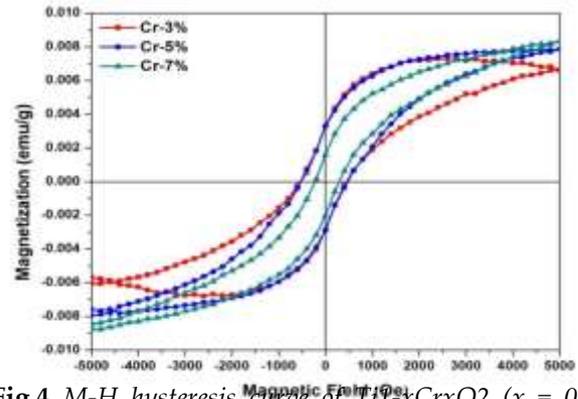

Fig.1 *Variation of real part of dielectric constant of Ti1-xCrxO2 (x = 0.00, 0.03, 0.05 and 0.07) NPs with frequency at room temperature.*
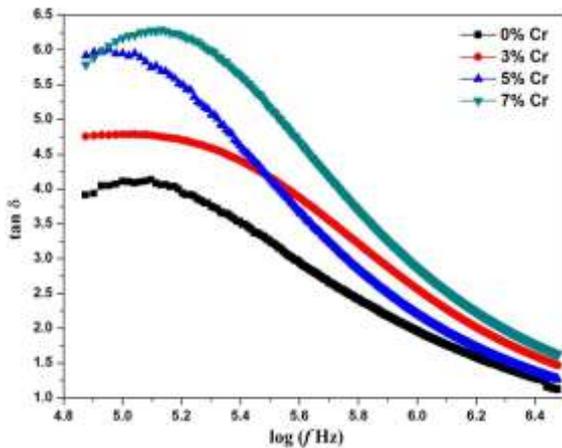
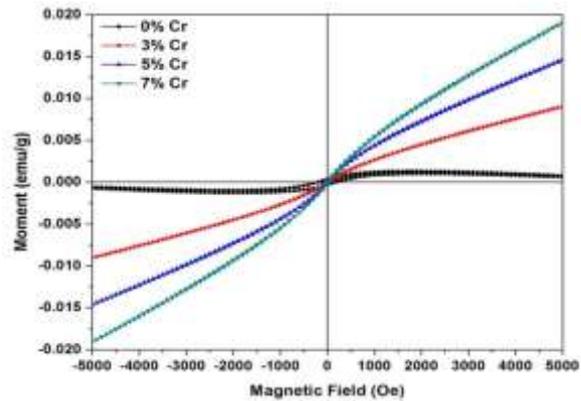**Fig. 2** *Variation of dielectric loss of Ti1-xCrxO2 (x = 0.00, 0.03, 0.05 and 0.07) NPs with frequency at room temperature.*
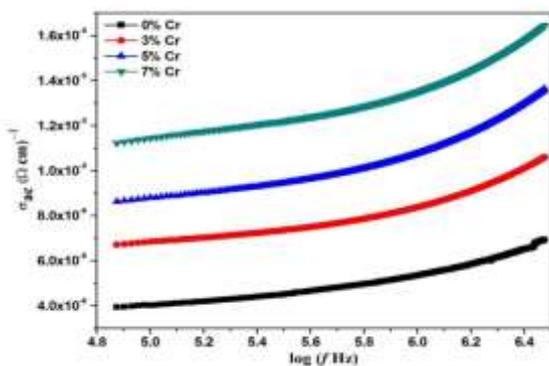
Fig. 3 *Variation of a.c. conductivity of Ti1-xCrxO2 (x = 0.00, 0.03, 0.05 and 0.07) NPs with frequency at room temperature.*

Fig.4 *M-H hysteresis curve of Ti1-xCrxO2 (x = 0.03, 0.05 and 0.07) NPs at room temperature.*

Fig. 5 *Experimental M-H variation of Ti1-xCrxO2 (x = 0.00, 0.03, 0.05 and 0.07) NPs measured with SQUID magnetometer at 300 K.*

REFERENCES

1) S. D. Delekar, H. M. Yadav, S. N. Achary, S. S. Meena, and S. H. Pawar, Appl. Surf. Sci. **263**, 536 (2012).

2) C. Lee, P. Ghosez and X. Gonze, Phys. Rev. B **50**, 13379 (1994).

3) S. K. Kim, W. D. Kim, K. M. Kim, C. S. Hwang, and J. Jeong, Appl. Phys. Lett. **85**, 4112 (2004).

4) M. Z. R. Khan, D. C. Hasko, M. S. M. Saifullah, and M. E. Welland, J. Phys: Condens. Matter **21**, 215902 (2009).

5) G. Madras, B. J. McCoy and A. Navrotsky, J. Am. Ceram. Soc. **90**, 250 (2007).

6) H. Zhang and J. F. Banfield, J. Mater. Chem. **8**, 2073 (1998).

7) G. A. Battiston, R. Gerbasi, M. Porchia, and P. Marina, Thin Solid Films **239**, 186 (1994).

8) Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Ya. Koshihara, and H. Koinuma, Science **291**, 854 (2001).

9) S. A. Chambers, S. Thevuthasan, R. F. C. Farrow, R. F. Marks, J. U. Thiele, L. Folks, M. G. Samant, A. J. Kellock, N. Ruzycki, D. L. Ederer, and U. Diebold, Appl. Phys. Lett. **79**, 3467 (2001).

10) J. Y. Kim, J. H. Park, B. G. Park, H. J. Noh, S. J. Oh, J. S. Yang, D. H. Kim, S. D. Bu, T. W. Noh, H. J. Lin, H. H. Hsieh, and C. T. Chen, Phys. Rev. Lett. **90**, 017401 (2003).

11) S. R. Shinde, S. B. Ogale, J. S. Higgins, H. Zheng, A. J. Millis, V. N. Kulkarni, R. Ramesh, R. L. Greene, and T. Venkatesan, Phys. Rev. Lett. **92**, 166601 (2004).

12) S. R. Shinde, S. B. Ogale, S. Das Sarma, J. R. Simpson, H. D. Drew, S. E. Lofland, C. Lanci, J. P. Buban, N. D. Browning, V. N. Kulkarni, J. Higgins, R. P. Sharma, R. L. Greene, and T. Venkatesan, Phys. Rev. B **67**, 115211 (2003).

13) S. A. Chambers, S. M. Heald and T. Droubay, Phys. Rev. B **67**, R100401 (2003).

14) K. A. Griffin, A. B. Pakhomov, C. M. Wang, S. M. Heald, and K.M. Krishnan, Phys. Rev. Lett. **94**, 157204 (2005).

15) T. C. Kaspar, S. M. Heald, C. M. Wang, J. D. Bryan, T. Droubay, V. Shutthanandan, S. Thevuthasan, D. E. McCready, A. J. Kellock, D. R. Gamelin, and S. A. Chambers, Phys. Rev. Lett. 95, 217203 (2005).