

The Effect of Co Doping on Structural, Optical and Dielectric Behaviour of TiO₂ Nanoparticles

Harpreet Singh Mahal, Bhanu Partap Singh, and Ravi Kant*

Department of Metallurgical and Materials Engineering, Punjab Engineering College, Chandigarh - 160 012, India

*E-mail: kravi.iitr@gmail.com

ABSTRACT

Chemical precipitation method was used to synthesise pure and Co-doped TiO₂ nanoparticles. The synthesised nanoparticles were studied for its structural optical and dielectric properties. X-Ray diffraction (XRD) confirmed the anatase phase with the tetragonal structure obtained for both samples. No extra peak was obtained in the pattern indicates that cobalt ions were successfully incorporated. The crystallite size of both samples were determined by using Debye-Scherrer's method, and it was found that it decreases with the dopant addition. UV vis spectroscopy was performed to study the optical properties of both samples. The dielectric constant (ϵ'), dielectric loss and ac conductivity (σ_{ac}) of both samples were studied against the frequency. The dielectric constant, dielectric loss and ac conductivity results showed that Co-doping has a significant effect.

Keywords: Co-doped TiO₂ nanoparticle; XRD; UV Vis; Dielectric and electrical properties

1. INTRODUCTION

In the past decade, the size dependent optical and electrical properties of semiconductor nanomaterials have received much attention due to numerous applications in the field of electronics. Semiconducting metal oxide nanomaterials with high dielectric constant and low dielectric loss have attracted the researcher because of their significant effect on their optical, electrical and magnetic properties. These characteristics features are greatly tuned by varying their crystallinity, particle size and morphology. Among the oxides, TiO₂ is the promising material due to its potential applications in microelectronic devices and micro communication systems. Now, the current technology demands nano sized components due to miniaturisation of microwave devices. The development of TiO₂ nanoparticles have the potential to satisfy the above requirements. Several techniques have been employed to improve the properties and functioning of TiO₂ by introducing the different dopants or thin film formation or changes the morphology.

Different studies have been reported that the doping of various elements to semiconducting material leads to modify the morphology, particle size and crystallinity. Wang¹, *et al.* observed that Ni doping to TiO₂ leads to improve the crystallinity and magnetisation. However, it is also observed that doping induces the substantial modification in optical and electrical of semiconducting materials.

Franco², *et al.* investigated the influence of Co-doped ZnO nano-particulate powders which enhances the dielectric constant. Mardare³, *et al.* have observed that effect of doping in dielectric properties of TiO₂ thin films and reported the

enhanced dielectric constant upon Nb doping due to the structural difference. Co-doped TiO₂ nanoparticles⁴ have studied significantly due to their increased photocatalytic activity, but dielectric and optical properties are rarely reported.

In this paper, the research work is focused on the study of structural, optical and dielectric characteristics of pure and Co-doped TiO₂ nanoparticles.

2. EXPERIMENTAL PROCEDURE

Chemical precipitation method was used to prepare pure and Co-doped TiO₂ nanoparticles. We used titanium isopropoxide (C₁₂H₂₈O₄Ti) for raw precursor material. Initially, 15 ml titanium isopropoxide was mixed slowly into 24 ml deionized water which causes the hydrolysis of the alkoxide and formation of hydrous titanium oxides precipitates. It was stirred at 40 °C for 30 min using magnetic stirrer. After that, a white precipitate was settled down at the bottom of the beaker and then filtered. It was separated by the centrifugation and washed with methanol and deionized water and dried with a temperature of 80 °C for 12 hours. The obtained fine white powder of TiO₂ nanoparticle was subjected to calcinations at the temperature 500 °C to eliminate possible impurities and the final powder was obtained. To prepare the Co-doped TiO₂ nanoparticles, the same steps were repeated by using cobalt sulphate (2%) as dopant precursor.

The calcined powders were examined by X-ray diffractometer (Bruker D8 Advance) with Cu K α radiation. The samples were scanned in the angle ranging 20° to 80° to determine the crystal structure and phases. The obtained results were analysed by using PAN analytical X'Pert PRO software.

UV-visible spectroscopy (Hitachi UV-3300) was used to identify the absorption peak in the range 300–900 nm.

The powder samples were taken and mixed with 5% PVA (Poly-Vinyl Alcohol). PVA acts as a binder and was mixed with sample powders in mortar pestle. After mixing, pellets were made using hydraulic press under pressure of 5 MPa. After pelletisation, the sintering of the samples was done at 700 °C to provide strength to the pellets. The dielectric properties were examined by using an LCR meter ZM2376 instrument (NF Corporation, Japan) at 10Hz– 3 MHz.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

Figure 1 represents the XRD patterns of pure and Co-doped TiO₂ nanoparticles. The different peaks assigned to planes (101), (004), (200), (105), (211), (204), (116), (220), and (215) were noticed in both samples. The anatase phase was confirmed in the observed peak positions which indicates the tetragonal structure of TiO₂. The experimental data was well matched with JCPDS card No. 01-071-1169. However, the doping of TiO₂ with Co leads to broadening of the peaks which can be ascribed to the reduction of crystallite size and enhancement of compressive lattice strain. However, XRD pattern of Co-doped TiO₂ sample does not show any peak corresponding to cobalt phase indicating that Co is uniformly distributed among the crystallite of TiO₂.

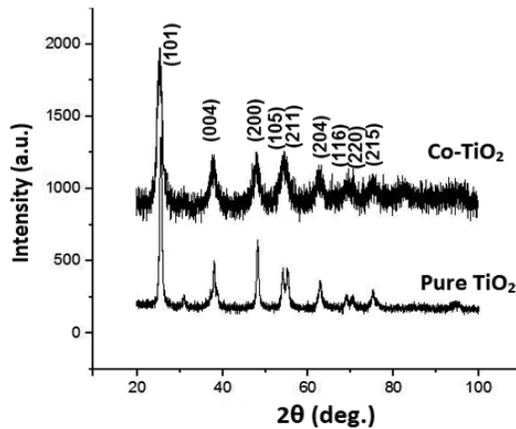


Figure 1. XRD patterns of pure and Co-doped TiO₂ nanoparticles.

From the above observed peaks of both samples, Debye–Scherrer formula was used to estimate the average crystallite size, the Eqn (1)

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where D is the crystallite size, k is constant, λ is the wavelength used ($\lambda=1.54 \text{ \AA}$), β is the full width at the half maximum (FWHM) and θ is the reflection angle. In comparison with pure TiO₂, the Co-doped shows a reduction of the crystallite size. This reduction in the crystallite size may be explained by the fact that the small shift in the peak position of doped samples towards the higher angle due to the variation in the lattice constant.

It is observed that the ionic charge of Co (+2) and Ti (+4) are different, thus the dopant incorporation leads to the creation of a vacancy of oxygen to maintain a charge neutrality. The dopant atoms, as well as the vacancy at the grain boundary, disturb the lattice structure and lead to effect the crystallinity after dopant addition. It is further noticed that the dopant addition also leads to the slight increase in the lattice parameter as listed in Table 1. An increase in the lattice parameter is expected as the ionic radius of Ti⁴⁺ ions (0.61 Å) is smaller than Co²⁺ (0.65 Å)⁵.

Table 1. The crystallite size and lattice parameters of pure and Co-doped TiO₂ nanoparticles.

Samples	Lattice constant		Crystallite size (nm)
	a (Å)	c(Å)	
Pure TiO ₂	3.7866	9.4680	11.9
Co-TiO ₂	3.7870	9.4434	7.5

3.2 Optical Properties

The optical properties of pure and Co-doped TiO₂ nanoparticles were explored by using UV-Vis absorption spectroscopy. It is observed that the absorbance characteristic is significantly influenced by numerous factor such as oxygen deficiency, particle size, defects in synthesised materials, etc.^{6,7}. Therefore, a red shift for Co-doped TiO₂ nanoparticles was noticed which signify that the optical properties of TiO₂ nanoparticle has significantly affected by Co dopant (Fig. 2(a)).

The band gap energy of synthesised TiO₂ nanoparticles was evaluated by using Tauc's formula^{6,8}.

$$\alpha h\nu = B (h\nu - E_g)^n \quad (2)$$

where α is absorbance, λ is wavelength (nm), $h\nu$ is energy of photon and E_g is the band gap.

The band gap energy was evaluated by extrapolating the linear region of $(\alpha h\nu)^2$ vs $(h\nu)$ plot to cut the photon energy i.e. x-axis as shown in Fig. 2(b). The value of the band gap for pure TiO₂ nanoparticle was estimated around ~ 3.09 eV. The red shift of Co-doped TiO₂ nanoparticle was further supported by its lower value ~ 3.02 eV. The above result confirms that the band gap energy of TiO₂ nanoparticle is reduced by Co dopant addition.

The reduction in the band gap energy is mainly attributed to the interaction between the localised d-electrons of Co (+2) which substituting Ti (+4) ions and band electrons of TiO₂⁹. In Co-doped TiO₂ sample, the substitution of Co (+2) on Ti (+4) leads to the strong crystal force due to neighboring oxygen ions. This strong crystal field interaction further splits d-band states of Co (+2) into the ground and excited states. The splitting of these states give rise to d-d electronic transition which lies in the visible range. Tauc's plot shown in Fig. 2(b) indicates the reduction in the band of doped TiO₂ sample further indicates the substitution of Co (+2) for Ti (+4) in TiO₂ lattice.

3.3 Dielectric Properties

From the Fig. 3(a), it is clear that the dielectric constant shows the decreasing trend with frequency. This is ascribed to the polarisation of the material that changes as the frequency

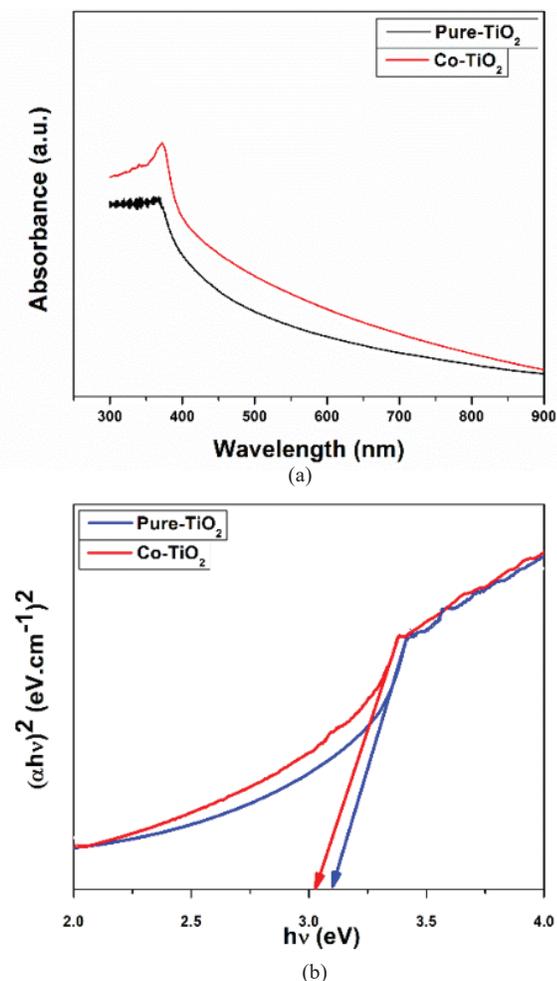


Figure 2. (a) UV Vis absorption spectra of pure and Co-doped TiO_2 nanoparticles and (b) Tauc's plot showing the band gap of pure and Co-doped TiO_2 nanoparticles.

gradually reaches higher values. At the low values of frequency, the polarisation is mostly due to space charge ionisation, but as it reaches the higher value, the polarisation changes to ionic polarisation which leads to reduce the dielectric constant. However, Co-doped sample shows the lower value of the dielectric constant because the doping results in excess concentration of electrons at outer most shells which oppose the electric field quite actively and thereby decreasing the value of the dielectric constant in comparison to pure TiO_2 sample.

Generally, dielectric constant reduces with increasing frequency, but a decrease of the dielectric constant with Co doping at the low frequency was noticed. This decrease is mainly ascribed to reduce grain size and different polarisation mechanism. Now in the case of nanomaterials, the polarisation was imparted by the hopping mechanism among carriers between the localised states, space charge polarisation, and the resultant displacement of dipoles under the influence of the applied field. Koops¹⁰ recommended that the grain boundaries have a significant effect at lower frequencies. Therefore, Co doping in TiO_2 may coagulate the grain boundary, leads to lower polarisation and thus dielectric constant decreases. Gafoor¹¹, *et al.* have reported similar results, where dielectric constant decreases upon doping of Ag in TiO_2 .

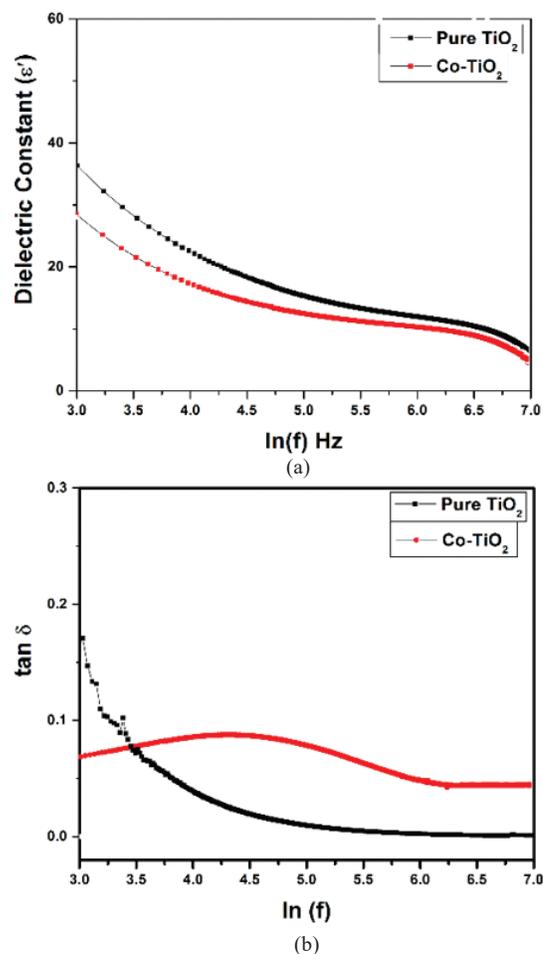


Figure 3. (a) Deviation of the dielectric constant against the frequency of pure and Co-doped TiO_2 nanoparticles and (b) Deviation of dielectric loss tangent against the frequency of pure and Co-doped TiO_2 nanoparticles.

On the other hand, at the higher frequency region, the dielectric constant is independent of frequency. This is because of the failure of electric dipoles to follow the quick variation of the alternating applied field. This may further lead to the enhancement of the friction between them. As a result, heat is produced and internal viscosity of the system and hence, dielectric constant reduces. Further, at higher frequencies, the dielectric constant shows the reduction in value and is obvious due to lagging behind the applied field. After the certain frequency range, dipoles do not follow the alternating field and thus dielectric constant shows almost constant behaviour.

Now in the dielectric system, the energy dissipation can be related to loss tangent ($\tan\delta$) and considered to owing to domain wall resonance. The dielectric loss factor of both pure and doped TiO_2 nanoparticle with frequencies is shown in Fig. 3(b). It is evident that $\tan\delta$ values decrease with frequency due to space charge polarisation. Further, it is observed that loss becomes small when Co doping is done. The low loss at higher frequency region is generally linked to the relaxation process. It occurs when the hopping frequency of localised electric charge carriers is likely to be equal to the frequency of applied ac voltage.

The variation of ac conductivity with frequencies of pure and Co-doped TiO₂ nanoparticles is represented in Fig. 4. The conductivity gradually increases for both the samples with rising frequencies. The conductivity is found to be increased with frequency and is mainly attributed to the increasing movement of electrons with frequencies. The high conductivity at the large frequency values confirmed the hopping of charge carriers between localised states. These results have been further supported by Fe, Sm and Al doped TiO₂ nanostructures¹²⁻¹⁴.

There is a little increase in conductivity was noticed for Co-doped TiO₂ nanoparticles. This improvement in the conductivity of Co-doped sample is mainly due to an effective increase in charge carrier concentration involved in doping mechanism, hence conductivity was found to increase.

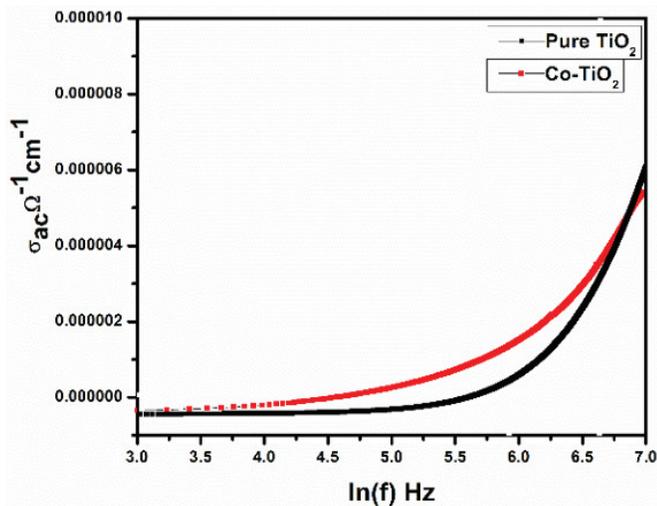


Figure 4. Deviation of ac conductivity against the frequency of pure and Co-doped TiO₂ nanoparticles.

4. CONCLUSIONS

In the present work, both pure and Co-doped TiO₂ nanoparticles were prepared by the chemical precipitation method. XRD results confirmed the anatase phase in both samples with no impurity phase indicates the successful incorporation of cobalt in TiO₂ lattice. Scherer's method was used to estimate the crystallite size and found that doping resulted decrease in crystallite size. UV-Vis absorption showed the red shift and intensity variation in the spectra of Co-doped sample. This also clearly indicated that incorporation of cobalt into TiO₂ lattice. Co-doped TiO₂ sample showed a low dielectric constant at low frequencies and become constant at higher frequencies. On the other hand, low dielectric loss was found in Co-doped sample at higher frequencies. The ac conductivity of Co-doped TiO₂ nanoparticle was also found to be increased due to the large number of charge carriers. This behaviour of materials make it suitable for dielectric and electronic applications.

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CONTRIBUTORS

Mr Harpreet Singh Mahal received his BTech (Metallurgical & Materials Engineering) from PEC (Deemed to be University) Chandigarh. Presently, he is working as Business Development Manager- Domestic and International at Bione Ventures Privtae Limited. His research interests include Nanomaterials Synthesis and characterisation, Dielectric, and optical materials.

He has contributed to prepare the doped Ag-TiO₂ nanoparticles and study their optical and dielectric properties.

Mr Bhanu Partap Singh received his BTech (Metallurgical & Materials Engineering) from PEC (Deemed to be University) Chandigarh. He has a keen interest in Nanomaterials and its dielectric and optical properties.

He has contributed to prepare the doped Ag-TiO₂ nanoparticles and study their optical and dielectric properties.

Dr Ravi Kant, did his MSc in Physics from G.N.D. University Amritsar and MTech in Nanoscience and Nanotechnology from Panjab University Chandigarh. After completing his masters, he joined as a research scholar at IIT Roorkee and completed the doctorate in 2015. Currently, he is working as Assistant Professor, Department of Metallurgical & Materials Engineering, PEC (Deemed to be University) Chandigarh. He has published more than 10 papers in international journals and in conferences. He evinces keen research interests in the area of: Composite Materials, Tribological behaviour, Doped ZnO nanomaterials and its dielectric and optical properties.

He has also reviewed the work in the same field and given many valuable suggestions.