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Structural, Optical and Dielectric Properties of Cobalt doped TiO_2

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Abstract:

Cobalt doped Titanium Dioxide (TiO_2) were synthesized by a standard solid-state reaction method. The formation of the single-phase compound and its structural parameters were investigated by X-Ray diffraction (XRD). The anatase phases of the samples were confirmed by XRD. Diffraction that is attributable to anatase is clearly noticeable in all materials (JCPDS code: 21-1272). The crystallite size of the samples has been calculated using Debye-Scherrer and Williamson Hall plot method with the help of Xpowder. Both results show the crystallite size of the samples in nanometer. SEM image shows a spherical uniform shape of the particles. Photoluminescence (PL) was held at different excitation wavelength. PL emission spectra show broad spectra of 400 nm to 500 nm. The dielectric constant and loss has been evaluated as a mapping of frequency (100 Hz-1 KHz) at room temperature. Dielectric constants linearly decrease with an increase in the frequency and at high frequency it's stable.

Key Words: TiO_2 (Anatase phase), Co doped TiO_2, XRD, SEM, PL, Dielectric.

1. Introduction

Titanium dioxide (TiO_2) TiO_2 nanomaterials are used in a broad range of application such as photocatalysis, sensor devices, paints and dye-sensitized solar cell [1-3]. TiO_2 exists in three primary phases; anatase, rutile and brookite. Rutile is the stable phase [4,5]. Sr doped TiO_2 nanoparticles showed more enhanced photocatalytic activity than TiO_2 nanoparticles [6].

Dielectric properties of prepared anatase and rutile TiO_2 and Cobalt doped TiO_2 has shown that the primary conflict in the dielectric constant value is defined by oxygen content in TiO_{2-X}. It is found that high temperature phase transitions occur in anatase TiO_2 thin films [7-8, 11-12].
In the present work, we have studied the structural, optical and electrical behaviour of the pure TiO_2 and 5% Co-doped TiO_2.

2. Experimental & Characterization Detail

Cobalt (Co) doped Titanium Dioxide (TiO_2) has been synthesized by solid state reaction route, using high purity TiO_2 (99.9%, Rankem), Cobalt Oxide (CoO) (99.9%, Molychem). All the materials are of analytical grade and are used as received if mentioned otherwise. 5% Co-doped TiO_2 has been developed in this workplace. Precursor TiO_2 were calcinate at 450^0C for 2 hours in silica crucible in air atmosphere. The 5% Co-doped TiO_2 was mixed and grinded by agate mortar with pestle for one hour before each thermal treatment. The powder was calcined at 450^0C for 10 hours in silica crucible in air atmosphere. The process has been repeated for several times to ensure homogeneous state with single phase powder.

The formation of the single phase compound was confirmed via X-Ray powder diffraction (XRD) analysis performed using Philips Xpert Pro (using CuKα radiation, λ = 1.5406 Å). The syllable structure of the products was explored by using scanning electron microscopy (JEOL). Photoluminescence emission spectra taken by HORIBAJOBIN YVON FlouroMax-4 Spectroflourimeter. The resulting mixture was pressed into a pellet form by applying pressure around 7.5 tons/cm2 (747 MPa) using a hydraulic press. Now, these pellets were sintered at 425^0C for 10 hours and then electroded with silver paint for electrical measurement.

3. Result and discussion

3.1 X-ray diffraction analysis (XRD)

The analysis of X-ray diffraction spectra (Fig. 1) indicates that the nano-TiO_2 and Co-doped TiO_2 powder prepared by the standard solid state reaction method possesses the anatase fine crystalline structure of the samples. Diffraction that is attributable to anatase TiO_2 is clearly detectable in all materials (JCPDS code: 21-1272). Withal, the tops of the Cobalt are not present in as prepared samples; it is distinctly observed in XRD spectra. No crystalline phase involving cobalt carbonate, cobalt oxide can be observed from fig. 1. It can be seen that with increasing concentration of Co, the peak position of Co-doped TiO_2 shows a shift to higher angle, compared to the pure TiO2 XRD pattern, which indicated change in the lattice parameters. This phenomena presumably result from the substitution of Co ions with a small ionic radius of 0.58 Å for Ti (0.72 Å) sites. It can be concluded that Cobalt ions have inserted into the lattice of TiO_2 and locate at interstices or occupy some lattice sites of titanium.

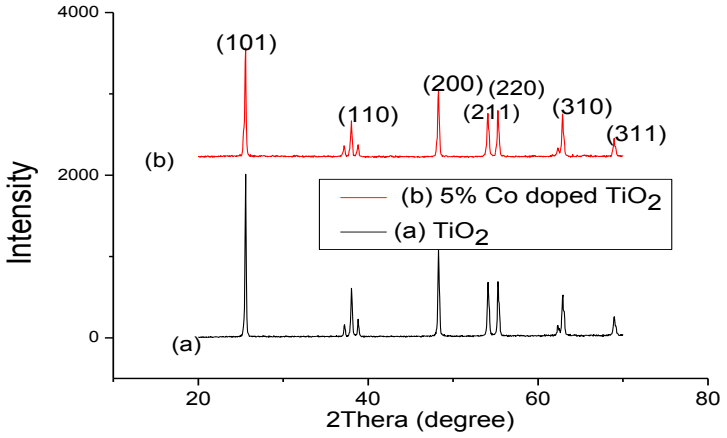

Figure. 1. XRD of the samples.

The crystallite size of the sample has been determined using the X-ray diffraction peak of the samples with the Williamson Hall plot method. Figure 2, Shows a Williamson Hall plot of the Co doped TiO_2 sample. The graph is plotted with the help of Xpowder and use the Lorentzian linear fitting method. This fitting facility is usable in the Xpowder software. The graph shows

the crystallite size of the samples. The crystallite sized of the sample calculated by the Debye Scherrer formula and Williamson Hall plot method is shown the figure 2. The crystallite size of the samples is observed in nanometer.

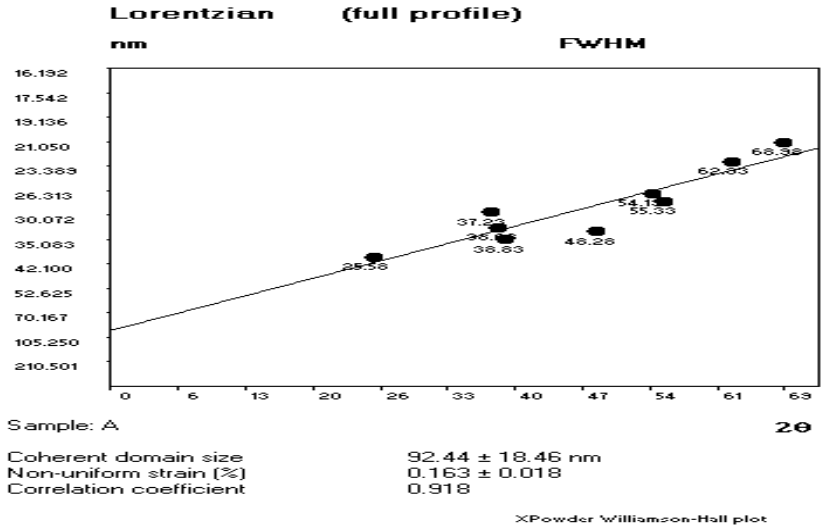

Figure. 2. The graph plot using Xpowder software for working out the crystalline size.

3.2 Scanning electron microscope (SEM)

The surface morphological properties of these compounds were investigated using SEM. The SEM micrographs indicate that the particle size is nearly uniform and spherical throughout the surface in each sample. The original anatase crystal grain size, measured by microscopic image process analysis was found of the order of near 200 nm. For a modest percentage of dopant concentration, the micrograph shows no significant change in word structure.

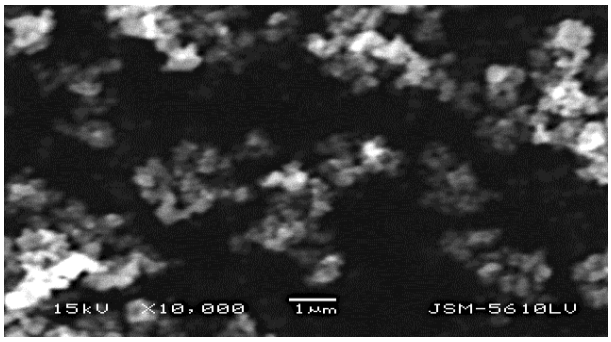

Figure. (2a). SEM micrograph of the TiO_2.

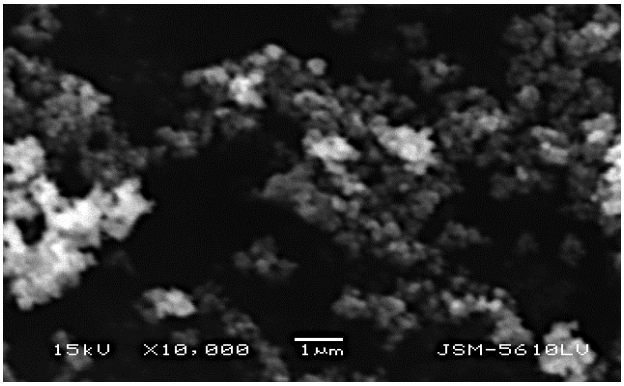

Figure. (2b). SEM micrograph of the Co doped TiO_2.

3.3 Photoluminescence Analysis

Fig. 3a and 3b shows the Photoluminescence spectra of the Pure TiO_2 and 5% Co doped TiO_2 at room temperature of the sample at the excitation wavelength of 302 nm and 330 nm respectively. The photoluminescence emission spectra have been taken with a filter (370 nm) and without filter.

Thither is a wide photoluminescence band in the wavelength range of 400-500 NM is observed at 302 nm and 330 nm excitation wavelengths. In the broad range of excitation wavelength the emission spectra do not indicate a shift in wavelength. The sharp peak is not observed, but broad emission spectra are observed at blue–green wavelength in both samples at the excitation wavelength of 302 and 330 nm. For better results, the photoluminescence mechanism of pure TiO_2 and Co doped TiO_2 needs further more investigations.

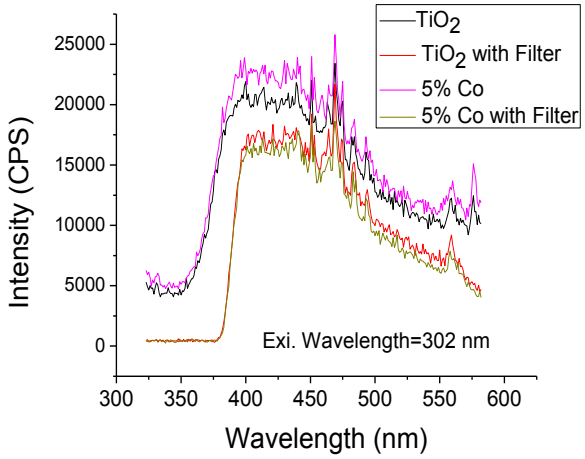

Fig. 3a. PL spectra of samples (Ex. Wavelength 302 nm)

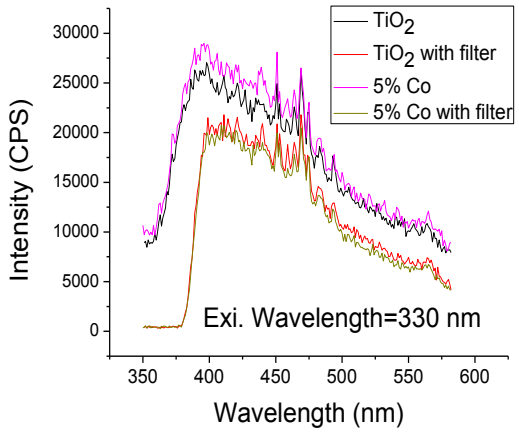

Fig. 3a. PL spectra of samples (Ex. Wavelength 330 nm)

3.4 Dielectric Analysis

Fig. 4a and Fig. 4b shows the variance of the dielectric constant and dielectric loss of the TiO_2 and 5% Co doped TiO_2 at room temperature with regard to frequency. It is clear that dielectric constant and dielectric loss decreases rapidly with increasing the frequencies. This variation of dielectric constant at lower frequencies is attributed not due to the electronic and ionic contribution, merely due to the space charge contribution. Spell with the increment of frequency, the ionic and electronic contribution becomes dominant and space charge

contribution diminishes gradually and hence dielectric constant decreases with the increment of frequency and attains an almost constant value (relaxation behavior) at higher frequencies.

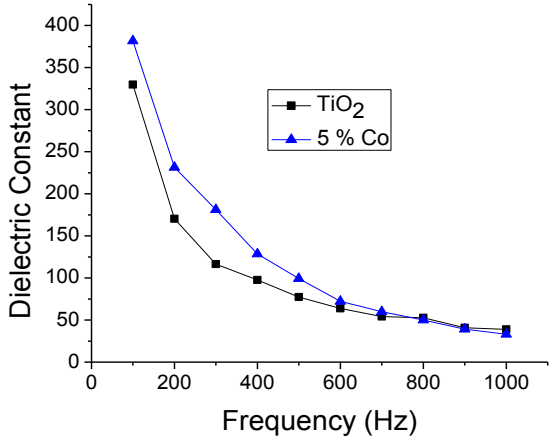

Fig. 4a. Dielectric Cont. Vs Frequency of the sample.

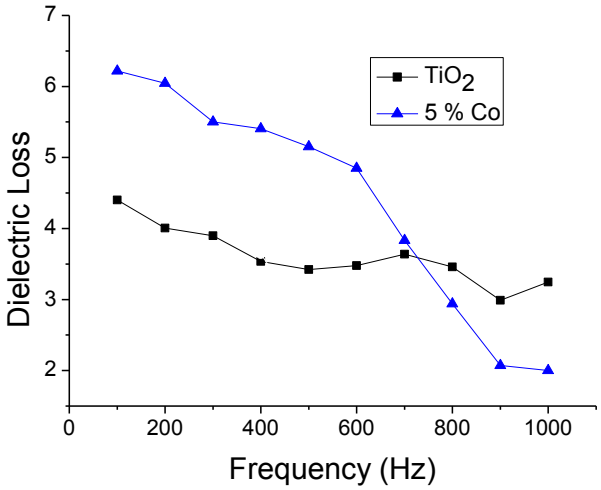

Fig. 4b. Dielectric loss Vs Frequency of the sample.

4. Conclusion

The XRD Data shows the crystalline structure of the sample. The XRD patterns of the peak position of Co-doped TiO_2 shows small shifts to higher angle compare with the pure TiO_2 XRD pattern. SEM micrograph shows a globular form. PL spectra observed a broad range of emission spectra. At the highest frequency dielectric constant decreases. Cobalt doped TiO_2 shows the effect on the PL and electrical properties.

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