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Electrical properties of pure and Zn^{2+}, Ni^{2+}, Cd^{2+} doped TiO_2 nanocrystals

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ABSTRACT

Pure and Zn^{2+}, Ni^{2+}, Cd^{2+} were introduced as dopants in the titanium dioxide by using simple microwave irradiated solvothermal technique and were synthesized as small crystallite sizes. Nanomaterials shows the pronounced electrical property due to the variation in the size. TiO_2 shows high electrical conductivity which was due to intrinsic defects created by oxygen vacancies in the TiO_2 lattice. Zn^{2+}, Ni^{2+}, Cd^{2+} which was introduced in the TiO_2 lattice increased the conductivity of TiO_2 due to the increase in donor concentration. The variation of electrical properties of Pure and Zn^{2+}, Ni^{2+}, Cd^{2+} introduced as dopants in the TiO_2 lattice with respect to temperature is discussed in this present study.

Keywords: TiO_2 nanocrystals, Microwave irradiated solvothermal technique, DC electrical analysis & AC electrical analysis.

1. INTRODUCTION

Oxide nanomaterials have unique electrical, physical, mechanical properties as they are size dependent than the bulk materials which have constant physical properties. Among the oxide nanomaterials Titania nanoparticles have wide applications in optical devices, sensors, and photocatalysis (Harizanov O and Harizanova A 2000; Li, 2003). The band structure of the nanoparticles can be modulated due to the decrease in the size of the nanoparticles and the energy levels get discreted. Due to this effect nanoparticles have specific properties. Semiconductor nanomaterials possess unexpected optical properties (Alivisatos, 1996) in LED's, biological labels, optoelectronic devices and solar cells. Semiconductor nanomaterials have wide field of applications which attracts the scientists to do research in this specific area. The variation of electrical properties of pure and Zn^{2+}, Ni^{2+}, Cd^{2+} introduced as dopants in the TiO_2 lattice with respect to temperature and their dielectric studies at 30-150 ºC with fixed 1 kHz frequency is discussed in this present study.

2. MATERIALS AND METHODS

Pure and TiO_2:Zn^{2+}, TiO_2:Cd^{2+} and TiO_2:Ni^{2+} doped nanocrystals prepared by simple microwave irradiated solvothermal technique (Chitra and Easwaramoorthy, 2014). The electrical measurements were made using disc shaped pellets and annealed for two hours at ~150ºC. The annealed samples were coated with silver paint to obtain a good conductive surface layer.

The electrical conductivity (Direct current) measurements were made by using the conventional two-probe technique at the temperature ranging from 30-150 ºC (Praveen & Mahadevan, 2005; Mahadevan & Jeyakumari, 2008; Selvarajan & Mahadevan, 2006).

HP 3457A Digital multimeter (Resistance range: 30Ω to 3GΩ) was used to measure the resistances of the prepared nanomaterials. The resistance could be measured after annealing nanomaterials at temperature ~160ºC and the reading should be taken while cooling the sample. Travelling microscope was used to measure the dimension of the pellets (Least count =0.001cm) (Saravanan, Pukazhselvan, & Mahadevan, 2011; Saravanan, 2012).

The electrical conductivity (Direct current) of the prepared nanomaterials was found out by using the formula.

$$\sigma_{dc} = \frac{d}{RA} \quad \text{mho m}^{-1}, (1)$$

'R' - Resistance of the sample
'd' - sample thickness
'A' – Area of the sample

Agilant 4284A LCR meter was used to measure the capacitance (C) and dielectric loss factor of the prepared nanomaterials to an accuracy of ± 1 % in the temperature range of 30 - 150 ºC and with fixed 1 kHz frequency.

For AC conductivity measurements the similar procedure was used and the reading should be taken while cooling the sample. The dielectric constant of the sample was found out by using the formula

$$\varepsilon_r = \frac{C}{C_{air}}. (2)$$

C_{air} – Capacitance of air
C - Capacitance of the sample
ε_r – Dielectric constant

3. RESULTS AND DISCUSSION

Electrical Measurements (DC): The calculated DC conductivity (σ_{dc}) of pure and Zn^{2+}, Ni^{2+}, Cd^{2+} introduced as dopants in the titanium dioxide nanocrystals was given in Figure 1. DC conductivity (σ_{dc}) of pure and Zn^{2+}, Ni^{2+}, Cd^{2+} introduced as dopants in the titanium dioxide nanocrystals was found to increase with the increase in the temperature. Free carriers in a semiconductor did not have sufficient energy to jump from one level to another level at low temperatures. When the temperature increased slowly, electrical conductivity (DC) increases which is due to the increase in the carrier concentration in the conduction band (Condeles, 2007).

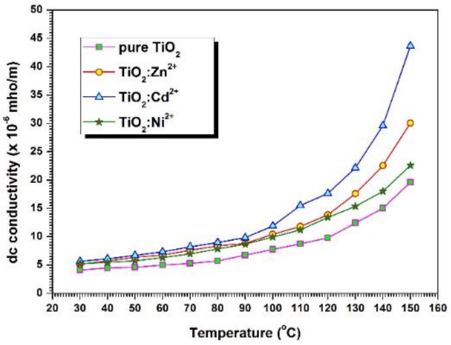


Figure.1.DC conductivities for pure and doped TiO_2 nanocrystals at different temperatures

At room temperature TiO_2 conducts electricity which was due to donor states introduced by the intrinsic defects created by oxygen vacancies in the TiO_2 lattice. Its properties were similar to ZnO (Springer, 2002; Gupta, 1992).

The variation of electrical conductivity in pure and Zn^{2+}, Ni^{2+}, Cd^{2+} introduced as dopants in the titanium dioxide nanocrystals was due to the intrinsic defects which was created by introduction of doped materials and also it depends upon the method of synthesis. The observed increase in the electrical conductivity (DC) clearly indicated that the Zn^{2+}, Ni^{2+}, Cd^{2+} doping affected the defect chemistry of the TiO_2. In the present study the electrical conductivity increases as the intrinsic donor concentration was increased due to introduction of Zn^{2+}, Ni^{2+}, Cd^{2+} in the TiO_2 lattice.

It was found in the present study that the (σ_{dc}) of pure TiO_2 was lower than the Zn^{2+}, Ni^{2+}, Cd^{2+} doped in the TiO_2 lattice. This was because that the dopant atoms (Zn^{2+}, Ni^{2+}, Cd^{2+}) perfectly occupy/replace the Ti^{2+} site in the crystal lattice of TiO_2 nanocrystals. Out of all these doped nanocrystals, (σ_{dc}) of Cd^{2+} introduced as dopant in the TiO_2 lattice was higher than the other doped nanocrystals.

The σ_{dc} values for the pure and Zn^{2+}, Ni^{2+}, Cd^{2+} doped in the TiO_2 lattice were fitted into the general equation for the temperature variation of conductivity given by

$$\sigma_{dc} = \sigma_o \exp\left[\frac{-\Delta E_{dc}}{kT}\right], \quad (3)$$

where ΔE_{dc} is the activation energy of the material, T is the absolute temperature of the sample and σ_o is a constant depending on the material.

$$\ln \sigma_{dc} = \ln \sigma_o - \frac{\Delta E_{dc}}{kT} \quad (4)$$

Values of Ln (σ_{dc}) plotted against 1000/T was shown in Figure 2. The slope of the straight line best fitted by least square analysis was used to calculate activation energy ΔE_{dc}. The intercept value obtained from the straight line was $\ln\sigma_o$. Table 1 indicates the values of the activation energy of pure and Zn^{2+}, Ni^{2+}, Cd^{2+} doped in the TiO_2 lattice.

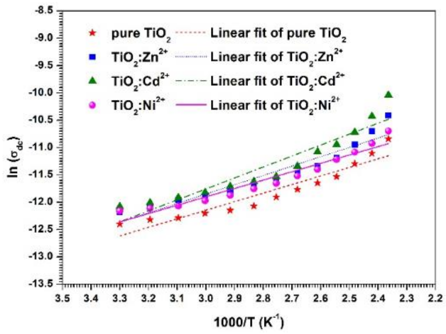


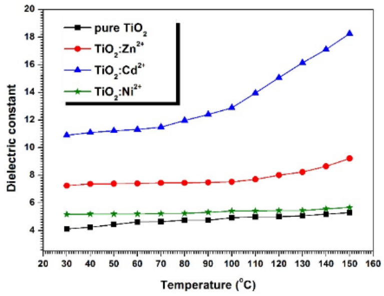
Figure.2.A plot of 1000/T *vs* Ln σ_{dc} for pure and doped TiO_2 nanocrystals for different temperatures

Table.1.DC activation energy values for pure and different dopant added TiO_2 nanocrystals

Sample name	$\Delta E_{dc} \pm 0.006$ eV
Pure TiO_2	0.135
TiO_2: Zn^{2+}	0.147
TiO_2: Cd^{2+}	0.173
TiO_2: Ni^{2+}	0.132

AC Electrical Measurements: The permanent or induced dipoles in the dielectric materials was due to the applied electric field. Among the electrical properties of the solids the dielectric constant was an important property. There exists a direct relationship between capacitance and dielectric constant of the nanomaterials (ε_r). Dielectric loss (tanδ) is the other important property of the nanomaterials. Dielectric loss is defined as the loss of power in a dielectric material by the application of voltage. Dielectric constant was defined as the ability to withstand the electric stress without any dielectric breakdown. The capacitance of the materials would be enhanced when the dielectric material was placed inside the condenser plates and the Dielectric constant measurement was based on the enhancement of capacitance of the materials.

The study of dielectric property with respect to temperature and frequency was very important to study various polarization of dipoles in the solids. (Hill, 1969; Basu, 1986; Gerhardt, 1986).



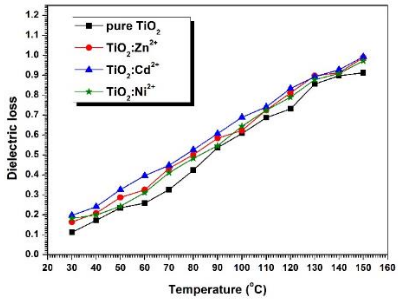


Figure.3&4.The variation of dielectric constants & dielectric loss with temperature at 1 kHz frequency for pure and different dopant added TiO_2 nanocrystals

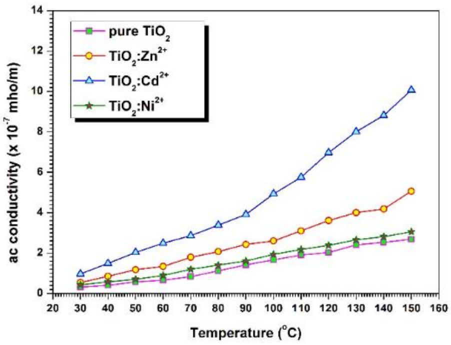


Figure.5.AC conductivities for pure and doped TiO_2 nanocrystals for different temperatures at 1 kHz frequency

Figure 3 & 4 showed the variation of dielectric constants & dielectric loss with temperature at 1 kHz frequency for pure and different dopant added TiO_2 nanocrystals.

The electrical conductivity (AC) was obtained by using the formula

$$\sigma_{ac} = \varepsilon_o \varepsilon_r \omega \tan\delta, \quad (5)$$

Where value of ε_o is 8.854 x 10^{-12} F/m (permittivity of free space)

ω is the angular frequency (ω = 2πf ; f = 1 kHz)

The figures 3-5 showed the variation of dielectric constant (ε_r), dielectric loss (tanδ) and electrical conductivity (AC) at the temperature ranging from 30 to 150°C. In the present study (ε_r), (tanδ) and σ_{ac} values increased with the increase in temperature. In the present study σ_{ac} values were lesser when compared to σ_{dc} values. The figures revealed that the introduction of Zn^{2+}, Ni^{2+}, Cd^{2+} doped in the TiO_2 lattice increased the values of (ε_r), (tanδ) and σ_{ac} than the undoped TiO_2 nanomaterials.

4. CONCLUSION

As the temperature increases the carrier concentration increases and hence the electrical conductivity (DC& AC) of pure and Zn^{2+}, Ni^{2+}, Cd^{2+} doped in the TiO_2 lattice increased. This was because that the dopant atoms (Zn^{2+}, Ni^{2+}, Cd^{2+}) perfectly occupy/replace the Ti^{2+} site in the crystal lattice of TiO_2 nanocrystals. It was concluded that among all the synthesized nanocrystals the electrical conductivity (AC & DC) of Cd^{2+} introduced in the TiO_2 lattice was higher than the other nanocrystals.

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