Chapter III
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Effect of doping of divalent and trivalent metal ions on the structural, electrical and photocatalytic behavior of nanosized semiconductor oxides

1. Introduction

Nanosized semiconductor oxides have attracted much attention due to their crucial roles in future technological applications. The fundamental properties of these nanomaterials such as physical, optical and electronic ones are greatly dependent on their shapes when their sizes are reduced to nanometer scale [1-5]. This is one of the most interesting as well as the most challenging aspect in the synthesis of semiconductor nanomaterials. In the recent times, a lot of effort has been put by the scientific community to develop novel methods to synthesize special nanostructures of the metal oxide semiconductor nanomaterials. It has been reported in the recent literature that unique morphologies exhibit superior electronic and photocatalytic properties than the conventional morphologies like nanoparticles, nanowires, etc. of the same material [6-9]. The utility of these materials has been extended by introducing additional properties, while retaining the existing properties. Methods for introducing new electronic magnetic and photocatalytic properties to semiconductor nanooxides are attracted an intense interest as prospects for nanotechnological applications emerge in the area of optoelectronics, photocatalysis etc. An effective method for manipulating the physical properties of the semiconductors involves impurity doping.

A great deal of attention has been given to doping of semiconductor oxides with divalent and trivalent metal ions. These doped nanomaterials have been demonstrated to show coexistence of different physical properties like semiconducting and photocatalysis [10-14]. Recently, semiconductor photocatalysts have attracted
extensive attention because of their potential application in decomposing all kinds of pollutants [15, 16]. Photocatalytic degradation of harmful dyes shows a good performance and could be used in the wastewater treatment domain. There are many reports in recent literature to have achieved photocatalysis in visible light region in these materials as a result of doping with two cations this would the dopants with lower valences many also lead to introduction of oxide vacancies. Whereas dopants with higher valence may remove the oxygen vacancies [17]. The change in the defects concentration by addition of dopants with larger / smaller valences is responsible for change in various physical properties. However it is with a great challenge to produce room temperature photocatalytic behavior. There have been an intense research still going on to the electronic and photocatalytic performance of semiconductor oxide.

Many studies were devoted to develop new semiconductor photocatalyst which can efficiently utilize solar light. Among all the semiconductor oxides, Cu$_2$O [18], Fe$_2$O$_3$ [19], Bi$_2$O$_3$ [20, 21], SrTiO$_3$ [22], CeO$_2$ [23] and V$_2$O$_5$ [24] have been widely studied for its interesting semiconducting and degrading organic pollutants under excitation of sunlight. So many efforts have been devoted to synthesis of these materials with different shape and size. It may be proposed that defects created as cation vacancy in the nanomaterial by the dopant ions contributed to give rise to semiconducting and photocatalytic properties. Here we doped divalent and trivalent metal ions on few semiconducting oxides such as bismuth oxide (Bi$_2$O$_3$), spinel cobalt oxide (Co$_3$O$_4$), vanadium pentoxide (V$_2$O$_5$), cuprous oxide (Cu$_2$O) and ceric oxide (CeO$_2$) to prepare a visible light driven photocatalyst, and investigated the crystalline phase, structure, morphology, semiconducting and dielectric properties. We found the photocatalytic activity of these doped oxide was increased on doping. In addition, the effect of doping on electrical conductivity and dielectric properties was also discussed.
2. Experimental

2.1 Synthesis of precursors

High purity metal salts of bismuth, cerium, cobalt and vanadium were used as starting materials. The required amounts of metal salts were dissolved in distilled water and then added disodium carboxylate solution at appropriate pH. Quantities of reactants were calculated according to the stoichiometry in the final product. The flow sheet diagram for dicarboxylate precursors and subsequent conversion to nanooxides is depicted in Fig. 1(a) and cuprous oxide was also synthesized by Benedict method and its flow sheet diagram is shown in Fig. 1(b).

2.1.1 Bismuth tartarate penta hydrate, $\text{Bi}_2(\text{C}_4\text{H}_4\text{O}_6)_{3.5}\text{H}_2\text{O}$

This precursor was prepared by the coprecipitation method by taking $\text{Bi(NO}_3\text{)}_{3.5}\text{H}_2\text{O}$ (10.410 g) in double distilled water (100 mL) The solution was placed in three necked flask under a stream of dry nitrogen atmosphere to prevent the air oxidation of ion. (Nitrogen was purified from traces of carbon dioxide and oxygen by passing the gas through empty trap then through sulphuric acid for removing moisture and then through alkaline pyrogallol and finally through a rap containing sodium hydroxide pellets with dry adsorbent cotton to get almost 99.8% pure nitrogen). The pH of the medium was adjusted to a low enough value (pH<5), so that hydroxide precipitate does not form. The solution was stirred vigorously with a magnetic stirrer. To this disodium tartarate (8.887 g dissolved in 50 mL distilled water) solution was then added slowly with stirring till a permanent precipitate occurred. Acetone was added in equal amounts to get more homogenous, stoichiometric, fine grained powders. The resultant precipitate of $\text{Bi}_2(\text{C}_4\text{H}_4\text{O}_6)_{3.5}\text{H}_2\text{O}$ was ivory in colour. The solution was filtered after stirring it for 30 minutes. The filtrate was checked for $\text{Bi}^{3+}$ solution by adding few drops of NaOH followed stannous chloride solution, not observed black ppt. whose absence
ensured complete coprecipitation. The precipitate was washed several times with cold distilled water and then with acetone to speed up the drying. It was air dried at the ambient temperature. Yield = 11.875 g.

Similar procedure was used for the synthesis of 10 wt% doped bismuth tartarate precursors by taking stoichiometric amount of samarium nitrate (0.487 g) and copper nitrate (0.265 g) as dopant.

Other dicarboxylate coprecipitates were prepared by following the procedure given above. The additional relevant details are summarized below.

2.1.2 Cerium tartarate mono hydrate, Ce\((C_4H_4O_6)_{1.5}\)\(\cdot\)H\(_2\)O

This precursor was prepared by taking Ce(NO\(_3\))\(_3\)\(\cdot\)6H\(_2\)O (12.614 g) in double distilled water (50 mL). To this disodium tartarate solution (12.030 g dissolved in minimum distilled water) was added slowly with stirring, till a permanent precipitate was occurred. The white precipitate was filtered and washed with distilled water and air dried at ambient temperature. Yield = 12.883 g.

Similar procedure was used for the synthesis of 10 wt% doped cerium tartarate by taking stoichiometric amount of nickel nitrate (0.444 g) and zinc nitrate (0.454 g) as dopant.

2.1.3 Cobalt tartarate dihydrate, Co\(_3\)\((C_4H_4O_6)_3\)\(\cdot\)2H\(_2\)O

This precursor was prepared by taking CoCl\(_2\)\(\cdot\)6H\(_2\)O (5.928 g) in double distilled water (50 mL). To this disodium tartarate solution (16.371 g dissolved in minimum distilled water) was added slowly with stirring, till a permanent precipitate was occurred. The faint pink precipitate was obtained. The precipitate was filtered and washed with distilled water and air dried at ambient temperature. Yield = 14.683 g.

10 wt% manganese and dysprosium doped cobalt tartarate was prepared by following same procedure by taking manganese (0.402 g) and dysprosium nitrate (0.928 g)
2.1.4 Ammonium oxy-vanadium carbonate, $\text{NH}_4\text{VO}_2(\text{CO}_3)_2$

This precursor was prepared by taking $\text{NH}_4\text{VO}_3$ (3.215 g) in hot double distilled water (50 mL). To this oxalic acid solution (6.931 g dissolved in 50 mL distilled water) was added slowly with stirring, after one hour stirring the precipitate was occurred. The precipitate was filtered and washed with distilled water and air dried at ambient temperature. The yellow coloured precipitate was obtained. Yield = 6.579 g.

10 wt% doped vanadium precursor was prepared by taking nickel nitrate (0.775 g) and gadolinium nitrate (1.230 g) as dopant in stoichiometric amount to get the final product.

2.1.5 Cuprous oxide precipitate, $\text{Cu}_2\text{O}$ (by Benedict method)

This was prepared by taking copper nitrate (18 gm) and mixture of sodium hydroxide and potassium sodium tartrate in 1:3 proportion. Mixture was then added in copper nitrate solution till precipitate occurred. Obtained precipitate was dissolved by adding excess mixture of sodium hydroxide and potassium sodium tartrate. To this glucose solution was added, boil the solution for five minute and cool to room temperature. Brown precipitate was obtained. It was air dried at the ambient temperature. Practical yield = 5.510 g.

The same procedure was used for 10 wt% doped $\text{Cu}_2\text{O}$ was prepared by taking manganese chloride (0.668 g) and ytterbium nitrate (1.211 g) as dopant.

2.2 Synthesis of undoped and doped nanooxide-semiconductors

The above undoped and doped precursors were decomposed and calcined slowly at 650 °C for two hours in a platinum crucible under static air atmosphere and then slowly cooled (3°C/ min) down to room temperature. This heat treatment was sufficient for achieving a complete decomposition of dicarboxylates. The powder obtained was polycrystalline. This sample was then reground and recalcined at the same
temperature for another two hours. The furnace was turned off and sample was removed at room temperature. The obtainable nanooxide samples such as Bi$_2$O$_3$, CeO$_2$, Co$_3$O$_4$, V$_2$O$_5$ and their respective doped nanooxides such as, Bi$_{1.9}$Sm$_{0.038}$Cu$_{0.062}$O$_3$, Ce$_{0.928}$Ni$_{0.028}$Zn$_{0.034}$O$_2$, Co$_{2.902}$Mn$_{0.049}$Dy$_{0.049}$O$_4$, V$_{1.91}$Ni$_{0.043}$Gd$_{0.047}$O$_5$, and were restored in a desicater. The brown precipitate of undoped and doped cuprous oxide was heated in oven at 120°C for 2h. The obtained Cu$_2$O and Cu$_{1.927}$Mn$_{0.036}$Yb$_{0.037}$O are also restored in desicater

2.3. Physical analysis

The experimental details for characterization of precursors and nanosized doped semiconducting oxides viz. C, H analysis, X-ray fluorescence spectroscopy (XRF), Energy dispersive X-ray analysis (EDAX), Far infrared spectroscopy, thermal analysis (TGA and DTA), X-ray powder diffraction(XRD), apparent density, scanning electron micrographs (SEM), direct current electrical conductivity, thermoelectric power, dielectric properties, UV-visible diffuse reflectance spectroscopy (UV-vis-DRS), and photocatalytic measurements are explained in chapter II.

2.4 Photocatalytic activity measurements

Photocatalytic activity of undoped and doped semiconductor oxides was evaluated by measuring the degradation of Victoria blue-B and Brilliant yellow in the aqueous solution under solar light irradiation. The detail set up and procedure for photocatalytic experiments are explained in chapter II.

Procedure: For each experiment, 50mg of semiconductor oxide was added to 50mL of 50mg/L of the Victoria blue-B or Brilliant yellow aqueous solution and dispersed under ultrasonic agitation for 5 min. The dispersion was magnetically stirred in dark to establish adsorption/desorption equilibrium between the sample and Victoria blue-B or Brilliant yellow dye. The solutions were then illuminated by solar light with constant
stirring (throughout the experiment) to induce a photochemical reaction. Aliquots (5mL) taken out at regular intervals of 20 min. and centrifuged to remove semiconductor oxide. The absorbance of Victoria blue-B or Brilliant yellow solution was determined using a UV-vis spectrophotometer (Shimadzu UV-1800) at the λ max of each dye. Then the percent degradation was calculated.

3. Results and Discussion:

3.1 Dicarboxylate and hydrolysed precipitation

Generally, during precipitation it is necessary to optimize the following conditions: (i) the mole ratio of different salts, (ii) the pH of the solution, (iii) the conditions such as solution temperature, the precipitate age time, the stirring etc. In literature, solubility data [25-26], when the individual tartarate or oxalate is precipitated the lowest yield result. To improve the yield of the precipitation of tartarate or oxalate, there is the possibility of applying organic solvent of low dielectric constant. In addition, the yield of precipitation of a metal tartarate or oxalate will be improved when precipitation is made together with less soluble metal tartarates or oxalates forming complexes. It has also suggested that the solubility product constant of all the constituents always exceed when the starting solution is added into the dicarboxylate ligand. Therefore, in the present study all precautions were taken for quantitative precipitation of two or three metal ions of high concentration from the respective metal salts of Bi, Ce, Co, V etc. solution by precipitation with disodium tartarates or oxalates at low enough pH ≤ 5 in the water- acetone mixture becomes possible. Here, the addition of acetone not only ensures a high yields, but also influences more homogenous, stoichiometric, fine-grained powders. The obtainable precursors crystalline powders whose colour depending on the nature of the ions. The experimental procedure is schematically shown in Fig. 1(a).
Cuprous oxide is also synthesized by Benedict method. The addition of Benedict solution, Cu (Tartarate), containing glucose which has aldehyde groups causes the reduction of copper ions resulting in the formation of brick red precipitate of Cu$_2$O. The experimental procedure is schematically shown in Fig. 1(b). The chemical reaction may be expressed in the following equation.

$$\text{RCHO} + 2\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{Cu}_2\text{O} + 4\text{H}^+$$

This method is advantageous because it could provide a time delay of more than five minutes before the reaction take place and or reactants can therefore, be thoroughly mixed. It is expected that the reactions begins and proceeds in a homogeneous environment.

### 3.2 Characterization of tartarate precursors

The composition of tartarate precursors i.e. bismuth tartarate pentahydrate Bi$_2$\((C_4H_4O_6)_3 \cdot 5\text{H}_2\text{O}\); cerium tartarate monohydrate, Ce\((C_4H_4O_6)_1.5 \cdot \text{H}_2\text{O}\); cobalt tartarate dihydrate, Co$_3$\((C_4H_4O_6)_3 \cdot 2\text{H}_2\text{O}\); and Ammonium vanadium carbonate, NH$_4$VO$_2$\((\text{CO}_3)_2\) are determined by elemental analysis. The elemental analysis in wt. % for these precursors and are very well match with the required ones. Further the x-ray florescence spectroscopy (XRF) analysis confirms the presence of the metal species in the same cationic ratio as initially used (See Table I). The presence of water of crystallization of these precursors is confirmed on the basis thermal analysis curves under static air atmosphere. These results are also further supplemented by Infrared spectra.

Infrared spectrum of these precursors are shown in Fig. 2. The probable band assignments of fundamental frequencies corresponding to tartarate or carbonate group, hydroxyl group, metal-oxygen bands etc. are given in Table II. The band at 3473 cm$^{-1}$ is assigned to the $\nu$(OH) vibration of water and secondary alcoholic grampus [27]. The width of this band confirms the presence of intramolecular hydrogen bands in these
complexes. The band at 3236 cm\(^{-1}\) for NH\(_4\)VO\(_2\)(CO\(_3\))\(_2\) corresponds to \(\nu\)N-H vibration of ammonium group in the compound. The strong band at 1406 cm\(^{-1}\) corresponds \(\nu\)C (for carbonates) present in this compound. The band at 1628 cm\(^{-1}\) and 1423 cm\(^{-1}\) are assigned to respectively. \(\nu\)\(_{asy}\) (OCO) and The \(\nu\)\(_{sy}\) (C=O) (Table II), Koppikar et al. [28]. observed that the bidentate coordination of the carboxylate group with the metal results in a lowering of both \(\nu\) (OCO) and \(\nu\) (C=O) frequencies due to the drainage of electron density from carboxylate group to the metal. However, at the same time a decrease in the O-C-O angle results in a decrease, in separation. Thus, infrared spectral analysis showed bidentate linkage to be more favorable for tartarate precursor on the basis of the difference between the antisymmetric and symmetric (C=O) stretching frequencies.

The infrared spectra in the range 1116-1058 cm\(^{-1}\) do not show any significant differences between tartaric acid and the metal complexes (i.e. precursors). From these results, it can be suggested that, there is no bonding with free C-OH group to metal in solid state [29-31]. Other bands which are all combination band may be assigned to the difference normal modes of vibrations of the carboxylate group [32, 33]

The \(\nu\) (M-O) vibrations are identified for the processors. They would suggest a six coordinate environment for the metal ion in the complex [34,35]. The insolubility of these precursors in both polar and non-polar solvents, would suggest the presence of polymeric octahedral structure [36, 37]. The fact that all the precursors are isolated as a powder and not as a single crystal meaning that no structural determination can be made. However, the infrared spectral data enable us to predict a possible stereochemistry for the tartarate. It is suggested that for metal-tartarate complexes, form between tartarate anion and metal ions are considered to have a planar arrangement with carboxylate group on each tartarate di-anion bonded to two different metal atoms.
to give a chain like polymeric structure. Oxygen atoms in adjacent layers to give a six-coordinate environment for the metal ion.

The TGA and DTA curve for tartarate precursor such as $\text{Bi}_2(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 5 \text{H}_2\text{O}$, $\text{Ce}(\text{C}_4\text{H}_4\text{O}_6)_{1.5} \cdot \text{H}_2\text{O}$, $\text{Co}_3(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_4\text{VO}_2(\text{CO}_3)_2$ under static air atmosphere are depicted in Fig. 3. The dehydration of these tartarate complexes except $\text{NH}_4\text{VO}_2(\text{CO}_3)_2$ compound can be detected on DTA curve at $\sim 90^\circ\text{C}$. The TGA curve show weight loss for dehydration step up to $180^\circ\text{C}$ corresponding to the loss of all water molecules in the complexes. The observed mass loss and corresponding temperature ranges are shown in Table III. The oxidative decomposition of these tartarate complexes was indicate by the presence of strong and broad exothermic peak on DTA curve at $291^\circ\text{C}$ while strong endothermic peak was observed on DTA curve for compound $\text{NH}_4\text{VO}_2(\text{CO}_3)_2$ Compound. The TGA curve showed one step weight loss in the temperature range 170-700$^\circ\text{C}$ corresponding to the formation of respective final oxide (Table III). The gaseous products obtained by thermal decomposition of these precursors were analyzed by qualitative gas detected method. The detailed detection procedure for CO, CO$_2$, C$_2$H$_4$ and C$_2$H$_2$ is described in chapter II. The thermal decomposition reaction of tartarate complexes may be written as follows:

a) Bismuth tartarate pentahydrate

$$\text{Bi}_2(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 5 \text{H}_2\text{O} \xrightarrow{50-170^\circ\text{C}} \text{Bi}_2(\text{C}_4\text{H}_4\text{O}_6)_3 + 5\text{H}_2\text{O}$$

$$\text{Bi}_2(\text{C}_4\text{H}_4\text{O}_6)_3 \xrightarrow{170-700^\circ\text{C}} \text{Bi}_2\text{O}_3 + 3\text{CH}_4 + 6\text{CO}_2 + 3\text{CO}$$

b) Cerium tartarate monohydrate

$$\text{Ce}(\text{C}_4\text{H}_4\text{O}_6)_{1.5} \cdot \text{H}_2\text{O} \xrightarrow{65-150^\circ\text{C}} \text{Ce}(\text{C}_4\text{H}_4\text{O}_6)_{1.5} + \text{H}_2\text{O}$$
c) Cobalt tartarate dihydrate

\[ \text{Co}_3(C_4H_4O_6)_3 \cdot 2\text{H}_2\text{O} \xrightarrow{35-230^0\text{C}} \text{Co}_3(C_4H_4O_6)_3 + 2\text{H}_2\text{O} \]

\[ \text{Co}_3(C_4H_4O_6)_3 \xrightarrow{230-650^0\text{C}} \text{Co}_3\text{O}_4 + 3\text{CH}_4 + 6\text{CO}_2 + 3\text{CO} \]

d) Ammonium vanadium carbonate

\[ \text{NH}_4\text{VO}_2(\text{CO}_3)_2 \xrightarrow{35-615^0\text{C}} \text{V}_2\text{O}_5 + \text{NH}_3 + \text{CO}_2 + \text{CO} \]

The TGA and DTA curve for cuprous oxide precipitate in static air atmosphere is shown in Fig. 3 (c). TGA curve show a weight gain up to 600\(^0\)C indicate cuprous oxide precipitate starts to oxidize to copper (II) oxide (CuO). A broad exothermic peak on DTA curve at around 450\(^0\)C, indicate that a oxidation reaction take place in this step to form CuO. The thermal reaction of the same may be written as

\[ \text{Cu}_2\text{O} \xrightarrow{35-600^0\text{C}} \text{CuO} + \text{Cu} \]

3.3.1 Compositional Analysis:

After characterizing the precursors were decomposed slowly at 650\(^0\)C for 2 hrs. in platinum crucible and then slowly cooled down to room temperature. There compounds are then reground and recalcined at the same temperature for another 2 hrs. The X-ray fluorescence spectroscopy (XRF) and energy dispersive X-ray analysis (EDAX) confirmed the presence of all the cations species were present in a perfect cation ratio (expected stoichiometry) in the calcined semiconducting oxides. (See Table IV). It is seen from EDAX spectra for all semiconducting oxides (Fig. 4 and 5) the dopant peak height relative to those of ion varied in the correct sense according to the
concentration of dopants expected by the nominal composition. The elemental composition analysis at several spot was uniform, which is indicative of a highly homogenous material (Fig. 4 and 5). This is due to the fact that all the cations are uniformly mixed. Compositional analysis obtained with these method could accurately quantify the different metal contents within ± 0.5wt% error, but it is unable to provide an accurate estimation of oxygen content.

3.3.2 X-ray diffraction studies:

X-ray diffraction pattern (XRD) of undoped and doped semiconductor oxides such as Bi$_2$O$_3$, Bi$_{1.9}$Sm$_{0.038}$Cu$_{0.062}$O$_3$, Co$_3$O$_4$, Co$_{2.902}$Mn$_{0.049}$Dy$_{0.049}$O$_4$, V$_2$O$_5$, V$_{1.91}$Ni$_{0.043}$Gd$_{0.047}$O$_5$, Cu$_2$O, Cu$_{1.927}$Mn$_{0.036}$Yb$_{0.037}$O$_3$, CeO$_2$ and Ce$_{0.938}$Ni$_{0.028}$Zn$_{0.034}$O$_2$ are presented in Fig. 6. The well resolved peaks observed in the XRD pattern indicate that all undoped and doped possess single phased. No second phase was detected in the XRD patterns of all the samples studies in the present work. The X-ray diffraction pattern is lower and broader in all doped semiconducting oxides. This indicates the growth of the crystalline grain is restricted by the doping ions, leading to the relative small grains. The experimentally observed the d-spacing values and relative intensities (Table V) are compared those reported in literature [38-42]. The lattice parameters are determined using the method of least squares to an accuracy of ± 0.002 nm and is shown in Table VI. These values are in perfect agreement with the data published in JCPDS File [38-42]. All the diffraction peaks are well assigned to the monoclinic structure of Bi$_{1.9}$Sm$_{0.038}$Cu$_{0.062}$O$_3$ samples, while cubic structure for Bi$_2$O$_3$, Bi$_{1.9}$Sm$_{0.038}$Cu$_{0.062}$O$_3$, samples, while cubic structure for Co$_3$O$_4$, Co$_{2.902}$Mn$_{0.049}$Dy$_{0.049}$O$_4$, Cu$_2$O, Cu$_{1.927}$Mn$_{0.036}$Yb$_{0.037}$O$_3$, and orthorhombic structure for V$_2$O$_5$ and V$_{1.91}$Ni$_{0.043}$Gd$_{0.047}$O$_5$. The incorporation of dopant into host lattice can cause a small shift of X-ray peak towards higher angle has been observed for strong peaks, which indicative of a slight
decrease in lattice parameter. This is due to a decrease of the defect concentration (i.e. oxygen vacancies; as required by the charge balance) [43-46]. This decrement may be due to the incorporation of dopant ions into lattice of host material [47, 48]. Again the peaks of doped samples show broadened which are explained on the basis of the small sizes of the nanocrystallites.

The XRD line width and particle size are connected through the Scherrer equation [49]. The crystallite size \( \langle D \rangle_{\text{X-ray}} = \frac{0.9 \lambda}{\beta \cos \theta} \) with \( \beta = \beta_a - \beta_b \), where \( \langle D \rangle_{\text{X-ray}} \) crystalline diameter \( \lambda \) is wavelength of the X-ray radiation is the measure of the broadening of diffraction due to size effect, \( \beta_a \) and \( \beta_b \) are the full-width at half-maximum of the XRD line of the sample and \( \theta \) is the Bragg’s angle. Using this relation, the observed mean values of crystallite size \( \langle D \rangle_{\text{X-ray}} \) are given in Table VI. As can be seen from this table the mean crystallite size of undoped and doped semiconductor oxides are in the range of 39.75 nm to 65.17 nm indicating the nanosized nature of the compounds.

From crystallite size \( \langle D \rangle \), total surface area \( A \) was determined by the following equation [50]

\[
\langle D \rangle = \frac{6 V}{A}
\]

Where \( V \) is the total volume of the crystallite i.e. determine from lattice parameter. The surface area of undoped and doped semiconductor oxides are listed in Table IV. The surface for these oxides are found in the range of 33.5m²/g to 65.0m²/g

3.3.3 Particulate properties

The X-ray density [51] of all compounds was determined using the formula \( D_x = \frac{8M}{Na^2} \)

where ‘M’ is the molecular weight (i.e. formula weight), ‘N’ is Avogadro’s number and ‘a’ is the lattice parameters. Also the porosity of the semiconducting oxides was
calculated using the relation \( P = (1 - D/D_x) \), where \( D \) and \( D_x \) are the apparent density and X-ray density respectively [52]. The results X-ray density (\( D_x \)), measured apparent density (\( D \)) and porosity (\( P \)) of undoped and doped semiconducting oxides are given in Table VI. It can be noticed that X-ray density of each sample is higher than the corresponding apparent density. This may be due to the existence of pores, which are formed and developed during semiconducting oxide preparation. Another reason for the presence of porosity may be the creation of more oxygen vacancies in doped samples as compared to undoped and as a result fewer cations are created [53]. The same observation is also seen in unit cell volume for each undoped and doped semiconducting oxides (see Tables VI).

Fig 7 and 8 showed the scanning electron micrographs (SEM) of \( \text{Bi}_2\text{O}_3 \), \( \text{Bi}_{1.9}\text{Sm}_{0.038}\text{Cu}_{0.062}\text{O}_3 \), \( \text{Co}_3\text{O}_4 \), \( \text{Co}_{2.902}\text{Mn}_{0.049}\text{O}_4 \), \( \text{Dy}_{0.049}\text{O}_4 \), \( \text{V}_2\text{O}_5 \), \( \text{V}_{1.91}\text{Ni}_{0.043}\text{Gd}_{0.047}\text{O}_5 \), \( \text{Cu}_2\text{O} \), \( \text{Cu}_{1.927}\text{Mn}_{0.036}\text{Yb}_{0.037}\text{O} \), \( \text{CeO}_2 \) and \( \text{Ce}_{0.938}\text{Ni}_{0.028}\text{Zn}_{0.034}\text{O}_2 \) oxides studied in the present work. The average grain size is estimated in the range of 35.96 nm to 65.08 nm for all compounds and the data is presented in Table VI. The morphology and spherical grain size of the samples seem to be non-uniform with somewhat agglomeration in the synthesized oxides which is unavoidable. Fig. 7 (e) show a SEM image of \( \text{V}_2\text{O}_5 \) show a rod type particles. As seen from Table VI, the particle size measured from XRD and SEM are in good agreement with each other.

### 3.3.4 Infrared Spectral Studies

The infrared spectra of undoped and doped semiconducting oxides, from which it can be seen that there are two strong and somewhat broad bands, \( \nu_1 \), at \( \approx 534 \text{ cm}^{-1} \) and \( \nu_2 \) at \( \approx 459 \text{ cm}^{-1} \) (See Table VI). These band are assigned respectively to the stretching and bending vibration of M-O and O-M-O in the octahedral coordination of the samples [54-56]. Also changes in the absorption bands each undoped and doped samples may
be interpreted as arising from the changes in bond distances. This phenomenon may be associated with stabilization each site. Since the crystal field stabilization energy for the cation of the same site and its charge depends on the bond distance. Therefore, it is suggested that ratio of the radius of the dopant ions into that of the host ion determine the crystal symmetry.

3.3.5 Electrical Conductivity Studies:

The temperature dependence of electrical conductivity of undoped, divalent and trivalent metal ion doped semiconducting oxides is depicted in Fig. 9. The experiments are repeated several times and the results are always found to be reproducible. The plot of log $\sigma$ against $T^{-1}$ obey the Arrhenius relation $\sigma = \sigma_0 \exp(-E_a/KT)$ indicating the semiconducting nature of all semiconducting oxides, where $E_a$ is activation energy, $\sigma_0$ is temperature independent constant, $K$ is Boltzamman constant and $T$ is absolute temperature. The values of log $\sigma$ were plotted against the reciprocal of absolute temperature. The slope of these lines was considered to give the activation energy ($E_a$) for the semiconductor of these oxides.

The room temperature conductivity value ($\sigma RT$) for all doped and undoped semiconducting oxides are found to vary between $4.63 \times 10^{-5}$ to $6.76 \times 10^{-11}$. The high conductivity value indicate that the elements with different oxidation state are present in these oxides. Also the presence of $M^{2+}$ ions and higher grain density result increase in conductivity [57] and small grain size and lower $Zn^{2+}$ and $Ni^{2+}$ content have the effect of decreasing the conductivity [58]. The log $\sigma$ vs $T^{-1}$ for undoped and doped $Bi_2O_3$, $Cu_2O$ and $CeO_2$ (Fig. 9) showed an initial decrease in electrical conductivity, except $V_2O_5$ compounds the temperature range 35 to $115^0C$; which corresponds to desorption of adsorbed water molecules, usually adsorbed water molecules behave as an electron donor. Then log $\sigma$ values are increased with increasing temperature for these Oxides.
This can easily interpreted in terms of increase in charge carriers (oxygen vacancies) of these compounds i.e. hoping of small polarons from site to site. Because of the strong interaction of the current carries with the lattice vibrations deformation potential at the given site must influence the electrical conductivity. According to Heyne [59], local electroneutrality is necessary, leading to a movement of electrons or holes beside the ionic flux. The activation energy (Ea) are calculated by applying the above relation to Fig. 10 and the results are listed in the Table VII. While log σ vs T^{-1} for undoped and doped Co₃O₄ showed two distinct slope with a break temperature around 458 K. This discontinuity can be attributed to a strong exchange interaction between the outer and inner electrons. The conductivity in Region A of these compounds are due to the lattice defect present (i.e. attributed to impurities), while conductivity in Region B is due to a thermally activated mobility of charge carriers [60] in the undoped and doped Co₃O₄ compounds. The two activation energies (Ea) are calculated for the two regions around break points and the results are listed in Table VII. It is noticed that the activation energy in the Region B is higher than that in the Region A. It can be associated with extrinsic surface defect migration in Region A; while in the Region B it can be increase in charge carriers (oxygen vacancy) of these compounds.

3.3.6 Thermoelectric Power Measurements:

Thermoelectric power measurements for all compounds (Fig. 10(a) and (b)) showed n-type semiconductor except Cu₂O,Co₃O₄ and its doped compounds have p-type semiconductor [See Table VII] The initial decrease of negative carrier (up to 400 K) might be due to desorption of the adsorbed water molecules on the particle surface. For temperature above 460K, its magnitude increase as the temperature increases except undoped and doped V₂O₅ compounds, which corresponding to the conduction mechanism via oxygen vacancies leads to an electronic conduction of n-type charge
carriers. While undoped and doped V$_2$O$_5$ samples showed the conduction by hopping of electron from divalent cation to trivalent cations. Verwey and deBoer [61] have established that in these oxides containing one ion of variable valence, the conduction take place via activation of states involving cation change valence as M$^{2+}$ = M$^{3+}$ and vice versa. In contrast for undoped and doped Cu$_2$O and Co$_3$O$_4$ showed a hole-mediated conduction mechanism seems to be dominant i.e. p-type semi conductivity throughout the temperature (up to 750K).

3.3.7 Dielectric Studies:

Fig. 11 and 12 showed the variation of dielectric constant ($\varepsilon'$) and dielectric loss (tan $\delta$) with frequency in the range 1 to 200 KHz for undoped and doped semiconducting oxides. The dielectric constant ($\varepsilon'$) and dielectric loss (tan $\delta$) i.e. dissipation factors decreases with increasing frequencies and reaching constant in particular frequencies. The large value at lower frequency is due to the predominance of interfacial dislocations, oxygen vacancies, grain boundary defects etc. [62]. While the decrease in dielectric constant ($\varepsilon'$) and loss (tan $\delta$) with frequencies is natural because of the fact that any species contributing to polarizability is bound to show logging behind the applied at higher and higher frequencies. The variations of dielectric constant and loss (tan $\delta$) with the frequencies reveals on the basis of space charge polarization due to inhomogeneous structure as per interfacial polarization [63] in agreement with Koops phenomenological theory [64]. Thus polarization as well as increasing conductivity, and activation energy (Ea) are affecting the dielectric constant ($\varepsilon'$) and dielectric loss (tan $\delta$).
3.3.8 Photocatalytic studies:

3.3.8.1 Band Gap Measurement:

As a UV-blocking material has strong absorption characteristics in the UV range. In order to investigate the photoabsorption properties of the prepared undoped and doped semiconductor oxides; the UV-vis diffuse reflectance were measured in the wave length range 300-500 nm. The diffuse reflectance spectrum (DRS) of these oxides are presented in Fig. 13 (a) and (b). The observed absorption peaks is due to charge transfer transition from anion (O$^{2-}$) to cation (M$^{2+}$), energy level in the metal oxide (MO).

The band gap plays a critical role in deciding the photocatalytic activity of photocatalysts for the reason that it participates in determining the $\frac{e^-}{h^+}$ recombination role. It was estimated by the diffuse reflectance absorption spectrum of undoped and doped semiconductor oxides by using following equation [65]

$$E_g = \frac{1240}{\lambda}$$

Where, $E_g$ is band gap energy of the photocatalyst in electron volts, and $\lambda$ is absorption edge wavelengths in nanometers. Band gap energy, $(E_g)$ was obtained by extrapolated intercept corresponding to wave length ($\lambda$) in nm. The corresponding band gap base on the UV absorption peak were found for undoped and doped semiconductor oxides and are depicted in Table VIII. As shown in Fig.13, the prepared semiconductor oxides are sensitive to visible light and can utilize visible light for degradating the dye in solution. The doped semiconductor oxides showed a remarkable absorption edge wavelength ($\lambda$) shift toward the longer wavelength region, which indicates a decrease of the band gap energy $(E_g)$ (See Table VIII). This might be due to the influence of numerous factors such as structural parameters, carrier concentrations and the presence of defects such
as oxygen vacancies, which may lead to the longer wavelength shift \([66]\). Another reason is that, on doping to semiconductor oxides, resulting in the formation of localized energy states that are closer to the conduction band \([67, 68]\) and thereby decreasing band gap. These results show that the undoped and doped semiconductor oxides have an obvious effect on their optical and catalytic properties.

3.3.8.2 Photodegradation studies on Victoria blue-B and Brilliant Yellow Solution

(a) Photolysis experiment

Before studying the various experimental parameters, the photodegradability was tested. The influence of solar light on the Victoria blue-B and Brilliant yellow dyes was investigated. When these dyes are exposed to solar light without the semiconductor oxide (i.e. catalyst) no significant change in concentration of these dye are observed even after 4 hr. This reveals that Victoria blue-B and Brilliant yellow does not undergo solar photolysis. These dyes are degraded completely in 4 hr. in the presence of undoped and doped semiconductor oxides. These changes were measured at 580 nm (\(\lambda_{\text{max}}\)) Victoria blue-B and 600 nm (\(\lambda_{\text{max}}\)) for Brilliant yellow by using Shimadzu UV-1800 spectrophotometer. The dye solutions were withdrawn at definite time intervals to determine the concentration of dye. The percentage removal of dye from the solution at different time intervals due to photodegradation was \(\% \text{ degradation} = \frac{C_0 - C_t}{C_0} \times 100\)

b) Effect of initial dye concentration

The effect of Victoria blue-B (10 to 100 mg/0.1L) and Brilliant yellow (10 to 40 mg/L) concentration on photocatalytic decolorization has been investigated by using solar light. The results shown in Fig 14 (a) and (a’) illustrated that the rate of photocatalytic decolorization of dyes was found to increase on increasing concentration up to Victoria blue B = 30 mg / 0.1 L and Brilliant yellow = 20 mg/L for Co\(_3\)O\(_4\), C\(_2\)O
and V₂O₅ oxides; while Victoria blue-B = 50 mg / 0.1 L, and 100 mg / 0.1L respectively for Bi₂O₃ and CeO₂ oxides and Brilliant yellow = 30 mg / L for both the oxides, similar result have been reported for the photocatalytic oxidation of other dyes [69-75]. The initial concentration dependence on the photodegradation rate of both the dyes may be due to the following reasons. When the dye concentration increases the amount of dye adsorbed on these catalytic surface increases. This effects the catalytic activity of the photocatalyst. The increase in dye concentration also decreases the path length of photon entering into the dye solution. At high dye concentration the dye molecules may absorb a significant amount of solar light rather than the catalyst and this may also reduce the catalytic efficiency [76].

c) Effect of amount of semiconductor oxides:

The amount of semiconductor oxides on the decolorization and degradation of Victoria blue-B solution (30 mg / 0.1 L) and Brilliant yellow sudation (20 mg/L) for Co₃O₄, C₂O and V₂O₅ while Victoria blue-B 50 mg / 0.1L and 100 mg / 0.1L solution respectively used for Bi₂O₃ and CeO₂ and Brilliant yellow (30 mg/L) solution used for Bi₂O₃ and CeO₂ were investigated by varying amount of these catalyst from 10 to 80 mg / 0.1 L. The percentage degradation of these dyes using solar light are illustrated in Fig. 14 (b) and (b’). The results demonstrate that the % degradation of Victoria blue-B dye increases linearly with catalyst loading up to 50 mg / 0.1 L. Above 50 mg / 0.1 L loading of catalyst % degradation decreases. Similarly the result for % degradation of Brilliant yellow increase. The enhancement of % degradation is due to (i) the increase in the amount of catalyst weight, which increases the number of dye molecules adsorbed (ii) the increase in the density of particles in the area of illumination. Above 50 mg / 0.1 L of catalyst, the % degradation is decreased. This may be due the enhancement of light reflectance by the catalyst particles and decrease in light
penetration [77-82]. Since the most effective % degradation of these dyes was observed with 50 mg / 0.1 L of all semiconductor oxides. Hence 50 mg / 0.1L was used as the catalyst loading for the photocatalytic reaction.

d) Effect of pH on dye degradation:

The most important parameter that influences the photocatalytic degradation is solution pH. The desired pH level was achieved by the addition of HCl (2M) and NaOH (2M) to the solution. The experiment was conducted using 50 mg semiconductor oxide and 50 mg / 0.1L Victoria blue-B solution. The pH of the supernatant solution adsorption was adjusted in the range 2 to 10 before photocatalytic degradation to know the effect of pH on Victoria blue-B degradation (using solar light) Fig. 14 (C). It has been observed that the % degradation of this dye increases on increasing the pH in the alkaline range. This can be explained on the basis that as the pH of medium is increased, there is a corresponding increase in the concentration of dimethyl amine ions. These dimethyl amine ions will adsorb on the surface of semiconductor oxides making it negatively charged which acts as an efficient trap for the photogenerated holes and hydroxyl radical are produced i.e.

\[
\text{OH}^-_{\text{surface}} + h^+_{\text{VB}} \rightarrow \cdot \text{OH}_{\text{surface}}
\]

Thus, there will be a cumbic attraction between semiconductor surface and cationic dye. This results in an increase of rate of % degradation of dye for all semiconductor oxide was used at pH = 8 for photocatalytic reaction similar behavior was observed by several authors [83-86].

Similarly, another experiment was conducted using 50 mg semiconductor oxide and 30 mg/ L of Brilliant yellow solution. The influence of pH value from 2 to 10 on % degradation of Brilliant yellow dye using solar light is shown in Fig. 14 (c’). It is
observed that % degradation of dye decreases with increase in pH up to 10. Therefore at acidic pH = 2.5 the % degradation is maximum for this dye. This could be ascribed to two reasons [83, 84]: Brilliant yellow is an anionic azo dye at low pH value, the agglomerated particles of semiconductor oxide reduces the dye absorption as well as photon absorption, and the azo linkage (-N = N-) is particularly susceptible to electrophilic attack by hydroxyl radicals. But at low pH the concentration of H\(^+\) is in excess and H\(^+\) ions interact with azo linkage decreasing the electron densities at azo group. Consequently, the reactivity of the hydroxyl radical by the electrophilic mechanism decreases. Thus, in an acidic medium photogenerated holes react with water molecules to produced hydroxyl radicals as give in following equation.

\[
\text{H}_2\text{O} + h^+_{\text{VB}} \rightarrow \cdot \text{OH} + \text{H}^+
\]

From the above fact, it is concluded that the photocatalytic reaction occurs not only on the catalyst surfaces but also in the close vicinity of the catalyst surfaces. Similar behavior was observed in previous studies [85-88]. The acid – base property of the metal oxide surfaces can have considerable implications upon their photocatalytic activity. Thus there result show that the degradation efficiency of undoped and doped semiconductor oxide photocatalyst was evaluated with solar light using Victoria blue – B at alkaline pH = 8.0 and Brilliant yellow at acidic pH=2.5 at room temperature.

**e) Effect of contact time:**

The photocatalytic activity depends on the ability of the catalyst to separate the electron-hole pairs. The rate of electron-hole pair separation and recombination is most significant factor in photocatalytic activity when a photon of solar light strikes the catalytic surface (i.e. on semiconductor oxide particle surface), the conduction band electrons and valence band holes separate. The electron then migrates to the catalyst
surface, where they react with free radicals and undergo secondary reactions leading to degradation of the dye [89]. The characteristic band for Victoria blue-B and Brilliant yellow centered at around 595 nm and 400 nm respectively in the temporal UV-vis spectra weakened immediately upon solar light irradiation, indicating degradation of the dye molecules.

The photocatalytic activity of undoped and doped semiconductor oxides were investigated by measuring the degradation of Victoria blue-B (50 mg/ 0.1 L at pH=8.0) and Brilliant yellow (30 mg/L at pH=2.5) in aqueous solution. Fig. 15 (a) depicts the % photodegradation of undoped semiconductor oxides such as Bi$_2$O$_3$, CeO$_2$, Co$_3$O$_4$, Cu$_2$OV$_2$O$_5$, and doped oxides such as Bi$_{1.9}$ Sm$_{0.038}$ Cu$_{0.062}$O$_3$, Ce$_{0.935}$ Ni$_{0.028}$ Zn$_{0.34}$ O$_2$, Co$_{2.902}$, Mn$_{0.049}$, Dy$_{0.049}$ O$_4$, Cu$_{1.927}$ Mn$_{0.036}$, Yb$_{0.037}$O and V$_{1.91}$, Ni$_{0.043}$, Gd$_{0.047}$, O$_5$ at 120 mn under solar light irradiation. As shown in fig. 15 (a) the percent of the photocatalytic degradation of both dyes were found to be increased with the increasing initial time (up to 90 min.) under solar light at first. But it decreased subsequently. The % degradation of Victoria blue-B and Brilliant yellow under solar light are depicted in Table VIII. It is interestingly noticed that the photocatalytic activity of doped semiconductor oxides are obviously higher than that undoped oxides. It is deduced that, doping of divalent and trivalent metal ions can introduced new electronic states in all semiconductor oxides to form an additional interband site [21, 23, 90-92]. The electron trapping by this interband site lead to the suppression of electron-hole recombination process and therefore efficient electron-hole separation is achieved on the photocatalyst surface. Therefore, doping with divalent and trivalent metal ions might have increased the rate of charge transport and flow of photogenerated electrons and holes on the semiconductor oxide surface, thereby increasing the photocatalytic degradation.
According to the published literature [21, 93, 94] we have proposed a mechanism for the enhanced photocatalytic activity of doped semiconductor oxides. It can be described as follows:

\[
\text{doped semi. oxide } + h\nu \rightarrow h_{VB}^+ + e_{CB}^-
\]

\[
\text{divalent dopant (M}^{2+} \text{) } + h^+ \rightarrow M^{3+} \text{ (hole trap)}
\]

\[
\text{trivalent dopant M}^{3+} + e^- \rightarrow M^{2+} \text{ (electron trap)}
\]

When semiconductor oxide is irradiated by solar light, hole \((h_{VB}^+)\) and electrons \((e_{CB}^-)\) are generated in its valence band and conduction band respectively. The photogenerated electrons and holes combine with divalent metal ion \((M^{2+})\) ions and simultaneously trivalent metal ions \((M^{3+})\) to form \(M^{3+}\) and \(M^{2+}\) ions respectively.

\[
M^{2+} + O \rightarrow M^{3+} + O_2^- \text{ (electron release)}
\]

\[
M^{3+} + OH^- \rightarrow M^{2+} + OH^- \text{ (hole release)}
\]

These superoxide anion \((O_2^-)\) and hydroxyl radicals \((OH^-)\) are powerful oxidizing species and it is degrade Victoria blue-B and Brilliant yellow dye.

The effects of various photocatalyst on photodegradation of Victoria blue-B and Brilliant yellow are shown in Fig. 15 (a). The result showed that CeO\(_2\) and CeO\(_{0.938}\), Ni\(_{0.028}\), Zn\(_{0.034}\) O\(_2\), Bi\(_2\)O\(_3\) and Bi\(_{1.9}\)Sm\(_{0.038}\) Cu\(_{0.062}\) O\(_3\) are more efficient than other undoped and doped semiconductor oxides. The order of activities of the photocatalysts are CeO\(_2\) > Bi\(_2\)O\(_3\) > V\(_2\) O\(_5\) > Cu\(_2\)O > Co\(_3\)O\(_4\). The similar trends are also observed for respective doped semiconductor oxides (See Table VIII). The high photoreactivity of CeO\(_2\) and Bi\(_2\)O\(_3\) and their doped compounds have been attributed to two factors; the slow recombination of the electron-hole pair and its large surface area. Other reason is that the CeO\(_2\) exhibits two valence state Ce\(^{3+}\) and Ce\(^{4+}\). Doping with Ni and Zn ions creates oxygen vacancies and the formation of Ce\(^{3+}\) and Ce\(^{4+}\), thereby a reduction of the
band gap. Similarly, Bi$_2$O$_3$ and its doped compound (Bi$_{1.9}$Sm$_{0.038}$Cu$_{0.062}$O$_3$) also show high photocatalytic activity due to the Bi$^{3+}$ with S$^2$ configuration and layer structure. In contrast to other undoped and doped semiconductor oxides might have the higher band transitions which are associated with the O$^2$-$M^{2+}$ (Lower valent metal ion) charge transfer processes, thereby decreasing the photocatalytic efficiency.

f) **Photodegradation Kinetics**

The Langumuir-Hinshelwood (L-H) kinetic equation has been used by several authors to analyze the heterogeneous photocatalytic reaction [95, 96].

The photodegradation of Victoria Blue-B and Brilliant yellow containing undoped and doped semiconductor oxides obeys pseudo-first order kinetics. At low initial dye concentration, the rate expression is given by following equation [95].

$$\frac{-d[C]}{dt} = k'[C]$$

Where K’ is the pseudo-first order rate constant. The dye is adsorbed onto the semiconductor oxide surface until adsorption desorption equilibrium is reached. After adsorption, the equilibrium concentration of the dye solution is determined and it is taken as the initial dye concentration for kinetic analysis. Integration of above equation (with the limit of C = Co at t = 0 with Co being the equilibrium concentration of the bulk solution) gives,

$$ln \left( \frac{Co}{C} \right) = k't$$

Where, Co is the initial concentration of Victoria blue-B or Brilliant yellow and C is the concentration at time ‘t’. A plot of ln Co/C versus t for photodegradation is shown in Fig.15 (b). A linear relation between both the dye concentration and solar light irradiation time has been observed. The rate constant was calculated by graphs (i.e. Fig.15 (b) as follows :
K = 2.303 x slope

The rate of degradation of Victoria blue-B and Brilliant yellow at the surface is proportional to the surface coverage of these dye on the photocatalyst (i.e. semiconductor oxide particles) assuming that these dye are strongly adsorbed on the catalyst surface than the intermediate products [97]. In L-H equation the rate constant k reflects the limiting rate of reaction at maximum coverage under the given experimental conditions of these dyes on the solar light illuminated photocatalyst.

The results of the rate constant (k) are given in Table VIII. It is observed that higher the rate constant (k), higher the percent photodegradation which enhance the rate of radical formation of hydroxy radicals (OH) and superoxide radicals (O_2^-). The pseudo first order rate constant (k) for Victoria blue-B show over all higher value than the Brilliant yellow (see Table VIII). This is due to the adsorption capacity for Victoria blue-B was slightly higher than Brilliant yellow. Other reason is that the structures of non-azo and azo dye may also contribute to the different percent degradation. The difference in term of molecular structure between the Victoria blue-B and Brilliant yellow (see Chapter II) is that the Victoria blue-B has a naphthalene ring substituted with two dimethyl amino phenyl group whereas Brilliant yellow has a terminal benzene ring is substituted with hydroxyl group. Both dimethyl amine and OH groups are strong electron donating groups and may cause the double bond or azo bond more active and can be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band. The difference on the electron-donating capacity of the aromatic compounds and their substitutions contribute to the photocatalytic degradation rate. The non-azo dye or azo dye molecules adsorbed on to the surface of semiconductor oxide by electrostatic attraction. The generated OH radicals or superoxide anion may attack the azo bond in Brilliant yellow and double bond in Victoria blue-B at the initial stage
and then mineralized completely as time increases in the solar light. Thus, the adsorption through dimethyl amine group of non-azo dye or terminal hydroxyl group and azo dye on to the surface of semiconductor oxide may be regarded as primary and critical steps toward efficient in the heterogeneous photocatalytic process [98].

**g) Measurement of the chemical oxygen demand (COD)**

In order to assess the degree of mineralization reached during the photocatalytic treatment; it’s based on the quantity of oxygen required to oxidize. The organic matter to form CO₂ and H₂O is generally determined. However in this case, the measurement of the chemical oxygen demand (COD) of the solar light irradiated solution are generally used for mineralization the parent azo or non azo dyes and its final product [99]. The molecular formulas of Victoria blue-B and Brilliant yellow are C₃₃H₃₂ClN₃ and C₂₆H₁₈Na₂O₈S₂ respectively. The stoichiometry equations of total oxidation for these dyes are shown below.

\[
C_{33}H_{32}ClN_3 + 45.5 \text{O}_2 \rightarrow 33 \text{CO}_2 + 15.5 \text{H}_2\text{O} + \text{HCl} + 3\text{NO}_3
\]  
(Victoria blue-B)

\[
C_{26}H_{18}Na_2O_8S_2 + 36 \text{O}_2 \rightarrow 26 \text{CO}_2 + 8\text{H}_2\text{O} + \text{H}_2\text{SO}_4 + 4\text{NO}_3 + \text{Na}_2\text{SO}_4
\]  
(Brilliant yellow)

The photocatalytic experiment was conducted by exposing of known concentration of Victoria blue-B and Brilliant yellow to solar light irradiation for 6h, and the clear samples were collected for COD analysis after removal of catalyst by centrifugation. The results of the tests are shown in Table VIII. The initial values of COD were agreed with the stoichiometry equations of total oxidation for Victoria Blue-B and Brilliant yellow, where the theoretical COD of Brilliant yellow is slightly higher than Victoria blue-B is shown in Table VIII, it was observed that the COD values decreases after photo oxidation under the solar light. By comparing the initial and final COD values it
is clearly that the photocatalytic process not only removed the color of azo dye or non-azo dye completely, but the intermediate products formed also being mineralized. Thus COD revel that complete mineralization of both dye after prolong irradiation with solar light.

**h) Mechanism of photodegradation:**

It is well known that the lifetime of photoexcited electrons are very less and hence the transfer of e\(^-\) to longer distance is kinetically prohibited. Therefore most photocatalysis happens in the near distance i.e. dye adsorbed on the surface of photocatalyst (i.e. semiconductor oxides) can only be degraded photocatalytically. The undoped and doped semiconductors will favor the interaction of the dye (adsorption) through hydrogen bonding on the surface of the catalyst (scheme A) and then undergo degradation during the solar light irradiation. In this way, the undoped and doped semiconductor oxides exhibit enhanced photodegradation to some extent. The above possible mechanism of photodegradation of Victoria blue-B and Brilliant yellow i.e. dye at semiconductor oxides (SC) is shown below (Scheme B):
Scheme B:

\[
\text{Dye} \xrightarrow{\text{hv}} \text{Dye}^* \\
\text{SC} \xrightarrow{\text{hv}} \text{SC} (e^{-}_{\text{CB}} + h^+_{\text{VB}}) \\
\text{SC} (h^+_{\text{VB}}) + \text{H}_2\text{O} \rightarrow \text{SC} + \text{H}^+ + \text{OH}^- \\
\text{SC} (h^+_{\text{VB}}) + \text{HO}^- \rightarrow \text{SC} + \text{OH}^- \\
\text{SC} + (e^{-}_{\text{CB}}) + \text{O}_2 \rightarrow \text{SC} + \text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2 \\
\text{Dye}^* + \text{OH}^- \rightarrow \text{Leuco [Dye]} \\
\text{Leuco [Dye]} \rightarrow \text{Degradation product}
\]

The undoped and doped semiconductor oxides utilizes the incident light absorbs a photon with energy greater than equal to the band gap energy to excite its electron from valence band to the conduction band thus leaving behind a hole. If this photogenerated charge separation is valid these electrons and holes could migrate to the surface of the semiconductor to react with adsorbed O\textsubscript{2} and H\textsubscript{2}O respectively.

This hole can abstract an electron from hydroxyl ions to generate hydroxyl radicals. In similar way there is a generation of superoxide radical anion. These hydroxyl radicals will then oxidize the dye to its leuco form, which may ultimately degrade to product. Thus the hydroxyl radical, superoxide radical anion, photogenerated holes and electrons selectively degrade, oxidize or reduce the dye molecules adsorbed on the surface of the semiconductor oxide particles (i)

Regeneration and recyclability of the semiconductor oxides

The undoped and doped semiconductor oxides were tested for their regeneration and recyclability up to four cycles after being used with sunlight using 50mg of the catalyst loaded with Victoria blue-B (50 mg /L) or Brilliant yellow (30 mg/L) from aqueous solution. The photocatalytic degradation capacity of these semiconductor oxides were reduced from 96% on the first cycle to 89% on the fourth cycle. From these
results it is clear that the undoped and doped semiconductor oxides (i.e. photocatalyst) are suitable for reuse.

4. Conclusions:

a) Undoped and doped semiconductor oxide such as Bi$_2$O$_3$, Bi$_{1.9}$Sm$_{0.038}$Cu$_{0.062}$O$_3$, CeO$_2$, Ce$_{0.938}$Ni$_{0.026}$Zn$_{0.034}$O$_2$, Co$_3$O$_4$, Co$_{2.902}$Mn$_{0.049}$Dy$_{0.049}$O$_4$, V$_2$O$_5$, V$_{1.91}$Ni$_{0.043}$Gd$_{0.047}$O$_5$, Cu$_2$O and Cu$_{1.927}$Mn$_{0.036}$Yb$_{0.037}$O are synthesized by precursor method and obtained at 650$^0$C. The composition of the cations were analysed by X-ray fluorescence (XRF) and energy dispersive X-ray (EDAX) spectroscopy.

b) X-ray diffraction of Bi$_2$O$_3$ and Bi$_{1.9}$Sm$_{0.038}$Cu$_{0.062}$O$_3$ possess a monoclinic structure, while Co$_3$O$_4$; Co$_{2.902}$Mn$_{0.049}$Dy$_{0.049}$O$_4$; Cu$_2$O, Cu$_{1.927}$Mn$_{0.036}$Yb$_{0.037}$O and V$_2$O$_5$; V$_{1.91}$Ni$_{0.043}$Gd$_{0.047}$O$_5$ have cubic and orthorhombic structure respectively. A slight decrease in lattice parameter is observed for all doped compounds. This is due to a decrease of the defect concentration (i.e. oxygen vacancies formation). The mean crystallite size of undoped and doped semiconductor oxides are in the range of 39.75 nm to 65.17 nm indicating the nano sized nature of the compounds.

c) The particulate properties like X-ray density, apparent density and porosity are determined for all compounds. The morphology and grain sizes for all compounds are determined by scanning electron micrographs.

d) The infrared spectrum for undoped and doped semiconductor oxides consist of two absorption bands associated with stretching ($\nu_1 = 534$ cm$^{-1}$) and bending vibration ($\nu_2 = 459$ cm$^{-1}$) of M-O and M-O-M respectively in the samples.

e) The temperature variation of d. c. electrical conduction for all semiconductor oxides showed a hopping of small polarons from site to site (i.e. increase in
charge carriers). The activation energy (Ea) was found to be extrinsic surface defect migration from room temperature to higher temperature (up to 650°C).

f) The thermoelectric power measurement confirms the undoped Bi$_2$O$_3$, CeO$_2$, V$_2$O$_5$ and their doped oxides have n-type semiconductors, while undoped and doped Cu$_2$O and Co$_3$O$_4$ oxides have p-type semiconductors.

g) The variation of dielectric constant ($\varepsilon'$) and dielectric loss (tanδ) with frequencies for all semiconductor oxides exhibit a space charge polarization due to the inhomogeneous structure as per interfacial polarization.

h) The band gap plays a critical role in deciding the photocatalytic activity of photocatalyst such as Bi$_2$O$_3$, CeO$_2$, Co$_3$O$_4$, V$_2$O$_5$, Cu$_2$O and their doped oxides was estimated by diffuse reflectance absorption spectrum. These semiconductor oxides are sensitive to visible light and can utilize visible light for degrading the dye in solution.

i) The photocatalytic process using solar light offers a valuable alternative for the degradation and mineralization of Victoria Blue-B and Brilliant yellow solution by using undoped and doped semiconductor oxides. The performance on photocatalytic degradation of Victoria blue-B and Brilliant yellow was enhanced with solar light irradiation a catalyst amount, initial dye concentration, pH, contact time, etc. have affected efficiency of degradation.

j) The pseudo first order rate constants showed that photocatalytic degradation of Victoria blue-B was more rapid than the Brilliant yellow dye which could be ascribed to the different molecular structure of the dyes and the adsorption capacity on the undoped and doped semiconductor oxides. The chemical oxygen demand (COD) showed complete mineralization of these dyes through the photocatalytic process, implying an environmental cleaning process.
5. References


38. JCPDS No. 27-0053.
39. JCPDS No. 81-0792
40. JCPDS No. 73-1701
41. JCPDS No. 85-0601
42. JCPDS No. 78-2076
50. L. Smart and E. Moore, solid state chemistry an introduction (2nd Edin, Chapman and Hall,1996) pp.79
64. C. G. Koops, Phys. Rev. 83 (1951)121.
**Table I**: Observed elemental and XRF data of undoped and doped precursor

<table>
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<tr>
<th>Precursor</th>
<th>Formula</th>
<th>Formula wt.</th>
<th>Elemental analysis in wt % (±0.5)</th>
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<td></td>
<td></td>
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<td>Req</td>
<td>Found</td>
<td>Req</td>
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</tr>
<tr>
<td>Bismuth tartarate pentahydrate</td>
<td>Bi$_2$(C$_4$H$_4$O$_6$)$_3$. 5H$_2$O</td>
<td>952.197</td>
<td>15.13</td>
<td>14.16</td>
<td>2.32</td>
<td>2.15</td>
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<tr>
<td>Cerium-tartarate monohydrate</td>
<td>Ce(C$_4$H$_4$O$<em>6$)$</em>{1.5}$.H$_2$O</td>
<td>380.253</td>
<td>18.95</td>
<td>18.10</td>
<td>2.12</td>
<td>2.10</td>
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<tr>
<td>Cobalt tartarate dihydrate</td>
<td>Co$_3$(C$_4$H$_4$O$_6$)$_3$. 2H$_2$O</td>
<td>657.036</td>
<td>21.93</td>
<td>21.55</td>
<td>2.45</td>
<td>2.40</td>
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<tr>
<td>Ammonium Vanadium carbonate</td>
<td>NH$_4$VO$_2$(CO$_3$)$_2$</td>
<td>220.994</td>
<td>10.86</td>
<td>10.82</td>
<td>1.82</td>
<td>1.19</td>
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<tr>
<td>Cuprous oxide precipitate</td>
<td>Cu$_2$O</td>
<td>143.091</td>
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<td>-</td>
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Table II: Infrared spectral bands and their probable assignments for Tartarate / oxalate precursors

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<tr>
<th>Bands for cm $\text{B}_i \text{C}_x \text{H}_y \text{O}_z \cdot \text{H}_2\text{O}$</th>
<th>Bands for cm $\text{C}e \text{C}_x \text{H}_y \text{O}_z \cdot \text{H}_2\text{O}$</th>
<th>Bands for cm $\text{C}o_3 \text{C}_x \text{H}_y \text{O}_z \cdot \text{H}_2\text{O}$</th>
<th>Bands for cm $\text{NH}_4\text{VO}_2 \text{CO}_3 \cdot \text{H}_2\text{O}$</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3473(s)</td>
<td>3427(m)</td>
<td>3429(s)</td>
<td>-</td>
<td>$\nu_{\text{stretching}}$ HOH</td>
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<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3236 (s)</td>
<td>$\nu_{\text{N-H}}$</td>
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<tr>
<td>1628(s)</td>
<td>1639(s)</td>
<td>1670(s)</td>
<td>1610(s)</td>
<td>$\nu_{\text{asy}}$ (C = O)</td>
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<tr>
<td>1423(s)</td>
<td>1413(s)</td>
<td>1491(s)</td>
<td>-</td>
<td>$\nu_{\text{sy}}$ (C = O)</td>
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<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1406 (m)</td>
<td>$\nu_{\text{C-O}}$ (carbonate)</td>
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<tr>
<td>1363(m)</td>
<td>1363(m)</td>
<td>1383 (m)</td>
<td>-</td>
<td>$\nu$ (C – C)</td>
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<tr>
<td>1276(m)</td>
<td>1282(m)</td>
<td>1290(m)</td>
<td>-</td>
<td>$\nu_{\text{sy}}$ C – O</td>
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<tr>
<td>1220(m)</td>
<td>1226(w)</td>
<td>1226(m)</td>
<td>1211 (m)</td>
<td>$\nu_{\text{asy}}$ C = O</td>
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<tr>
<td>1068(m)</td>
<td>1116(m)</td>
<td>1112(m)</td>
<td>1174 (m)</td>
<td>$\nu_{\text{C-O}}$ (alcohol)</td>
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<tr>
<td>1047(m)</td>
<td>1058(m)</td>
<td>1066(m)</td>
<td>1004 (m)</td>
<td>$\nu_{\text{sy}}$ (C – O),</td>
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<tr>
<td>999(m)</td>
<td>923(w)</td>
<td>933(w)</td>
<td>966 (w)</td>
<td>$\delta$ (O – C – O)</td>
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<tr>
<td>895(m)</td>
<td>831(m)</td>
<td>833(m)</td>
<td>833 (w)</td>
<td>$\nu_{\text{C-H}}$ wag</td>
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<tr>
<td>786(m)</td>
<td>709(m)</td>
<td>792(m)</td>
<td>732 (w)</td>
<td>$\nu_{\text{sy}}$ C – C</td>
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<tr>
<td>640(m)</td>
<td>623(m)</td>
<td>624(m)</td>
<td>667 (m)</td>
<td>$\nu_{\text{H–O–H}}$</td>
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<tr>
<td>599 (w)</td>
<td>572 (m)</td>
<td>538 ( s)</td>
<td>522 (w)</td>
<td>$\nu_{\text{(m–o)}, \nu_{\text{(C – C)}}}$</td>
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</table>

$s =$ small, $m =$ medium, $w =$ weak
Table III: TGA and DTA data of precursors under static air atmosphere

<table>
<thead>
<tr>
<th>Precursor</th>
<th>TGA</th>
<th>DTA peak temp. (°C)</th>
<th>Predicted intermediates and final products</th>
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<tbody>
<tr>
<td></td>
<td>% mass loss</td>
<td>Temp. range (°C)</td>
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<tr>
<td></td>
<td>Observed</td>
<td>Calculated</td>
<td></td>
</tr>
<tr>
<td>Bi$_2$(C$_4$H$_4$O$_6$)$_3$·5H$_2$O</td>
<td>9.21</td>
<td>9.27</td>
<td>50-170</td>
</tr>
<tr>
<td></td>
<td>44.03</td>
<td>45.95</td>
<td>170-700</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bi$_2$(C$_4$H$_4$O$_6$)$_3$</td>
</tr>
<tr>
<td>Ce(C$_4$H$_4$O$<em>6$)$</em>{1.5}$·H$_2$O</td>
<td>4.58</td>
<td>4.73</td>
<td>64-150</td>
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<tr>
<td></td>
<td>49.52</td>
<td>51.48</td>
<td>150-650</td>
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<td></td>
<td></td>
<td>90</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Ce(C$_4$H$_4$O$<em>6$)$</em>{1.5}$</td>
</tr>
<tr>
<td>Co$_3$(C$_4$H$_4$O$_6$)$_3$·2H$_2$O</td>
<td>5.47</td>
<td>5.80</td>
<td>40-150</td>
</tr>
<tr>
<td></td>
<td>61.22</td>
<td>60.16</td>
<td>150-650</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>110</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Co$_3$O$_4$</td>
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<tr>
<td>(NH$_4$)$_2$VO$_2$(CO$_3$)$_2$</td>
<td>16.08</td>
<td>17.69</td>
<td>234-615</td>
</tr>
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<td></td>
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<td>325</td>
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<tr>
<td>Precipitate Cu$_2$O</td>
<td>Weight gain</td>
<td></td>
<td>40-600</td>
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<td>450</td>
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<td>Cu$_2$O</td>
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Table IV: Observed XRF and EDAX analysis of undoped and doped semiconductor nanooxides

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<thead>
<tr>
<th>Compounds</th>
<th>Metal analysis in wt % (±0.5)</th>
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<tr>
<td></td>
<td>Metal</td>
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<tr>
<td></td>
<td>Bi</td>
</tr>
<tr>
<td></td>
<td>Sm</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ce</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
</tr>
<tr>
<td></td>
<td>CeO$_2$</td>
</tr>
<tr>
<td></td>
<td>Co</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td>Gd</td>
</tr>
<tr>
<td></td>
<td>V</td>
</tr>
<tr>
<td></td>
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<td>Mn</td>
</tr>
<tr>
<td></td>
<td>Yb</td>
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* The figures in parenthesis indicate metal analysis obtained from EDAX method.
**Table V**: X-ray diffraction data of undoped and doped semiconductor nanooxides

<table>
<thead>
<tr>
<th></th>
<th>Bi$_2$O$_3$</th>
<th>Bi$<em>{1.9}$Sm$</em>{0.038}$Cu$_{0.062}$O$_3$</th>
<th>CeO$_2$</th>
<th>Ce$<em>{0.93}$Ni$</em>{0.028}$Zn$_{0.003}$O$_2$</th>
<th>Co$_2$O$_4$</th>
<th>Co$<em>2$V$</em>{0.049}$Dy$_{0.006}$O$_4$</th>
<th>V$_2$O$_5$</th>
<th>V$<em>{1.9}$Ni$</em>{0.043}$Gd$_{0.006}$O$_5$</th>
<th>Cu$_2$O</th>
<th>Cu$<em>{1.9}$Mn$</em>{0.036}$Yb$_{0.007}$O</th>
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<tr>
<td>Observed 'd' spacing values of nano oxides (Å)</td>
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<tr>
<td></td>
<td>3.4635 (25)*</td>
<td>3.4741 (18)*</td>
<td>3.1314 (100) *</td>
<td>3.1293 (100) *</td>
<td>4.6622 (19)*</td>
<td>4.6573 (21)*</td>
<td>5.7564 (19)*</td>
<td>5.7490 (35)*</td>
<td>3.0174 (7)*</td>
<td>3.0055 (7)*</td>
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<td></td>
<td>3.3165 (33)</td>
<td>3.3092 (32)</td>
<td>2.7105 (28)</td>
<td>2.7073 (28)</td>
<td>2.8590 (38)</td>
<td>2.8537 (37)</td>
<td>4.3753 (100)</td>
<td>4.3753 (100)</td>
<td>2.4636 (100)</td>
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<td>3.2594 (100)</td>
<td>3.2524 (100)</td>
<td>1.9141 (51)</td>
<td>1.9141 (52)</td>
<td>2.4365 (100)</td>
<td>2.4327 (100)</td>
<td>4.0883 (27)</td>
<td>4.0958 (39)</td>
<td>2.1332 (38)</td>
<td>2.1329 (9)</td>
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<td></td>
<td>3.1907 (22)</td>
<td>3.1818 (31)</td>
<td>1.6332 (39)</td>
<td>1.6322 (40)</td>
<td>2.0197 (24)</td>
<td>2.0205 (20)</td>
<td>3.4062 (42)</td>
<td>3.4062 (85)</td>
<td>1.5074 (28)</td>
<td>1.5057 (26)</td>
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<td></td>
<td>2.7137 (40)</td>
<td>2.7073 (34)</td>
<td>1.5633 (7)</td>
<td>1.5628 (8)</td>
<td>1.6483 (10)</td>
<td>1.6456 (25)</td>
<td>2.8788 (26)</td>
<td>2.8806 (62)</td>
<td>1.2853 (20)</td>
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<td>2.6978 (37)</td>
<td>2.6899 (44)</td>
<td>1.3544 (7)</td>
<td>1.3541 (9)</td>
<td>1.5556 (21)</td>
<td>1.5481 (25)</td>
<td>2.7643 (19)</td>
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<td>1.2412 (13)</td>
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<td>2.6152 (26)</td>
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<td>2.3708 (28)</td>
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<td>1.2100 (10)</td>
<td>1.2322 (11)</td>
<td>1.2320 (14)</td>
<td>2.1873 (13)</td>
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<td>1.7834 (23)</td>
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<td>1.7275 (12)</td>
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<td>1.6755 (16)</td>
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<td>1.7834 (23)</td>
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*The figures in parenthesis are intensities relative to the line of highest intensity (100%)*
Table VI: X-ray diffraction data, particulate properties and infrared spectral data of undoped and doped semiconductor nanooxide

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Structure</th>
<th>Lattice constant 'a' nm</th>
<th>Mean crystallite size &lt;D&gt; X-Ray nm ±10%</th>
<th>Surface Area (m²/g)</th>
<th>X-Ray density Dₓ (g.cm⁻³)</th>
<th>Apparent density Dₓ (g.cm⁻³)</th>
<th>Porosity P=1-Dₓ/Dₓ</th>
<th>Average particle size (from SEM) nm</th>
<th>Unit cell volume (nm³)</th>
<th>Infrared spectral absorption band cm⁻¹</th>
<th>( ν_1 )</th>
<th>( ν_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₂O₃</td>
<td>Monoclinic</td>
<td>a= 0.580, b=0.820, c= 0.752</td>
<td>39.75</td>
<td>6.661</td>
<td>9.386</td>
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<td>0.700</td>
<td>39.78</td>
<td>0.329</td>
<td>692</td>
<td>501</td>
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<tr>
<td>Bi₁₋₀.₃₅Sm₀.₀₃₈Cu₀.₀₆₂O₃</td>
<td></td>
<td>a= 0.594, b=0.792, c= 0.754</td>
<td>40.78</td>
<td>6.346</td>
<td>9.254</td>
<td>1.946</td>
<td>0.789</td>
<td>43.50</td>
<td>0.327</td>
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<td>500</td>
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<tr>
<td>CeO₂</td>
<td>Cubic</td>
<td>0.541</td>
<td>43.44</td>
<td>1.429</td>
<td>7.192</td>
<td>0.596</td>
<td>0.917</td>
<td>41.09</td>
<td>0.158</td>
<td>690</td>
<td>466</td>
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<td>Ce₀.₉₃Ni₀.₀₂₈Zn₀.₀₃₄O₂₂</td>
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<td>0.541</td>
<td>63.33</td>
<td>1.692</td>
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<td>476</td>
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<td>Co₃O₄</td>
<td>Cubic</td>
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<td>1.393</td>
<td>0.770</td>
<td>64.85</td>
<td>0.527</td>
<td>646</td>
<td>547</td>
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<td>Co₂.₉₀₂Mn₀.₀₄₉Dy₀.₀₄₉O₄</td>
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<td>4.544</td>
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<td>0.518</td>
<td>671</td>
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<td>V₂O₅</td>
<td>Orthorhombic</td>
<td>a=0.356, b=1.149, c= 4.374</td>
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<td>35.96</td>
<td>0.179</td>
<td>653</td>
<td>470</td>
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<td>V₁₋₀.₁₉Ni₀.₀₄₃Gd₀.₀₄₇O₅</td>
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<td>a=0.357, b=1.149, c= 4.379</td>
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<td>12.132</td>
<td>3.464</td>
<td>1.666</td>
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<td>38.63</td>
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<td>0.583</td>
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<td>0.077</td>
<td>653</td>
<td>472</td>
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<td>1.763</td>
<td>0.723</td>
<td>48.56</td>
<td>0.077</td>
<td>640</td>
<td>472</td>
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Table VII: Electrical conductivity data of undoped and doped semiconductor nanooxides

<table>
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<tr>
<th>Compounds</th>
<th>Conductivity measurements</th>
<th>Thermoelectric power measurements</th>
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<td></td>
<td>Temp.range (K)</td>
<td>Activation energy Ea (ev)</td>
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<td>Bi2O3</td>
<td>304 - 833</td>
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<td>0.661</td>
</tr>
<tr>
<td>CeO2</td>
<td>303 - 714</td>
<td>0.690</td>
</tr>
<tr>
<td>Ce0.938Ni0.028Zn0.034O2</td>
<td>303 - 649</td>
<td>0.758</td>
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<td>Co3O4</td>
<td>Region A 326 - 458</td>
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</tr>
<tr>
<td></td>
<td>Region B 458 - 543</td>
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</tr>
<tr>
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</tr>
<tr>
<td></td>
<td>Region B 471 - 617</td>
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<td>V2O5</td>
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<td>0.217</td>
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<tr>
<td>V1.91Ni0.043Gd0.047O5</td>
<td>306 - 806</td>
<td>0.256</td>
</tr>
<tr>
<td>Cu2O</td>
<td>301 - 561</td>
<td>0.690</td>
</tr>
<tr>
<td>Cu1.927Mn0.036Yb0.037O</td>
<td>312 - 588</td>
<td>0.758</td>
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</table>
### Table VIII: Photocatalytic details of undoped and doped semiconductor nanooxides

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Adsorption edge λ (nm)</th>
<th>Band gap (eV)</th>
<th>% Degradation</th>
<th>Pseudo first order rate constant K (min⁻¹)</th>
<th>Chemical oxygen demand (COD) mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>VBB</td>
<td>BY</td>
<td>VBB</td>
</tr>
<tr>
<td>Bi₂O₃</td>
<td>412</td>
<td>3.00</td>
<td>98.29</td>
<td>74.93</td>
<td>0.032</td>
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<tr>
<td>Bi₀.₇Sm₀.₃Cu₀.₀₆₂O₃</td>
<td>417</td>
<td>2.97</td>
<td>98.38</td>
<td>82.20</td>
<td>0.035</td>
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<tr>
<td>CeO₂</td>
<td>354</td>
<td>3.50</td>
<td>98.64</td>
<td>74.98</td>
<td>0.033</td>
</tr>
<tr>
<td>Ce₀.₉₃₈Ni₀.₀₂₈Zn₀.₀₃₄O₂</td>
<td>358</td>
<td>3.46</td>
<td>99.61</td>
<td>85.68</td>
<td>0.038</td>
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<tr>
<td>Co₅O₄</td>
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<td>4.13</td>
<td>55.59</td>
<td>51.05</td>
<td>0.006</td>
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<tr>
<td>Co₂.₀₂₉Mn₀.₄₉₄Dy₀.₀₄₉O₄</td>
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<td>4.10</td>
<td>72.68</td>
<td>56.56</td>
<td>0.011</td>
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<tr>
<td>V₂O₅</td>
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<td>3.03</td>
<td>71.37</td>
<td>54.98</td>
<td>0.008</td>
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<td>V₁.₀₉₁Ni₀.₅₄₄Gd₀.₀₄₇O₅</td>
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<td>2.51</td>
<td>89.80</td>
<td>57.92</td>
<td>0.018</td>
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<tr>
<td>Cu₂O</td>
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<td>2.25</td>
<td>65.30</td>
<td>35.56</td>
<td>0.008</td>
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<tr>
<td>Cu₁.₀₂₇Mn₀.₀₃₆Yb₀.₀₃₇O</td>
<td>565</td>
<td>2.19</td>
<td>66.18</td>
<td>49.95</td>
<td>0.009</td>
</tr>
</tbody>
</table>

VBB-Victoria blue-B, BY-Brilliant yellow
Fig. 1: (a) Flowchart for the synthesis of semiconductor nanooxide powders by dicarboxylate method. (b) Flowchart for the synthesis of Cu$_2$O
Fig. 2: Infrared spectra of precursor
(a) Bi$_2$(C$_4$H$_6$O$_6$)$_3$·5H$_2$O, (b) Ce(C$_4$H$_6$O$_6$)$_1$.5H$_2$O, (c) Co$_3$(C$_4$H$_6$O$_6$)$_3$.2H$_2$O,
(d) NH$_4$VO$_2$(CO$_2$)$_3$, (e) Precipitate Cu$_2$O
Fig. 3: TGA and DTA curves for dicarboxylate precursor in normal air atmosphere.

(a) Bi$_2$(C$_4$H$_4$O$_6$)$_3$·5H$_2$O,  
(b) Ce(C$_4$H$_4$O$_6$)$_{1.5}$·2H$_2$O,  
(c) Co$_3$(C$_4$H$_4$O$_6$)$_3$·2H$_2$O,  
(d) NH$_4$VO$_2$(CO$_2$)$_3$,  
(e) Precipitate Cu$_2$O.
Fig. 4: Energy dispersive X-ray spectrum (EDAX) of undoped and doped semiconductors
(a) Bi$_2$O$_3$,  (b) Bi$_{1.9}$Sm$_{0.038}$Cu$_{0.062}$O$_3$,  (c) CeO$_2$, (d) Ce$_{0.938}$Ni$_{0.028}$Zn$_{0.034}$O$_2$,
(e) Co$_3$O$_4$,  (f) Co$_{2.902}$Mn$_{0.049}$Dy$_{0.049}$O$_4$
Fig. 5: Energy dispersive X-ray spectrum (EDAX) of undoped and doped semiconductors
(a) V$_2$O$_5$, (b) V$_{1.91}$Ni$_{0.043}$Gd$_{0.047}$O$_5$, (c) Cu$_2$O, (d) Cu$_{1.927}$Mn$_{0.036}$Yb$_{0.037}$O$_5$. 
Fig. 6: X-ray diffraction patterns of the undoped and doped semiconductor nanooxides.
Fig. 7: Scanning electron micrographs (SEM) of undoped and doped semiconductors
(a) Bi$_2$O$_3$, (b) Bi$_{1.9}$Sm$_{0.038}$Cu$_{0.062}$O$_3$, (c) CeO$_2$, (d) Ce$_{0.938}$Ni$_{0.028}$Zn$_{0.034}$O$_2$,
(e) Co$_3$O$_4$, (f) Co$_{2.902}$Mn$_{0.049}$Dy$_{0.049}$O$_4$
Fig. 8: Scanning electron micrographs (SEM) of undoped and doped semiconductors
(a) V$_2$O$_5$, (b) V$_{1.91}$Ni$_{0.043}$Gd$_{0.047}$O$_5$, (c) Cu$_2$O, (d) Cu$_{1.927}$Mn$_{0.036}$Yb$_{0.037}$O,
Fig. 9: Plot of log $\sigma$ against $T^{-1}$ of undoped and doped semiconductor oxides
Fig. 10: Plot of thermoelectric power, $\mu$ (volt k$^{-1}$) against temperature, $T$ (K) of (a) undoped and (b) doped semiconductor oxides.
Fig. 11: Plot for variation of dielectric constant ($\varepsilon'$) with frequency for (a) undoped (b) doped semiconductor oxides.
Fig. 12: Plot for variation of dielectric loss (tan \( \delta \)) with frequency for (a) undoped and (b) doped semiconductor oxides

(a) UNDOPED SEMICONDUCTOR OXIDES
(b) DOPED SEMICONDUCTOR OXIDES
Fig. 13: Plot of Reflectance (%) against wavelength (nm) for (a) undoped and (b) doped semiconductor oxides
Fig. 14: Effect of (a) and (a’) Dye concentration; (b) and (b’) Amount of catalyst; (c) and (c’) pH on the photocatalytic degradation of the Victoria blue-B and Brilliant yellow dye for solar light irradiation (time 90 min)
Fig. 15: (a) Photocatalytic degradation curves of Victoria blue-B and Brilliant yellow dyes over different irradiation time (b) Ln Co/C versus time graph for the decomposition of Victoria blue-B and Brilliant yellow dyes by undoped and doped semiconductor nanooxides.