Chapter IV
CHAPTER IV

Structural, Electrical and Photocatalytic Properties of Dual Doped Spinel Oxides Nano Particles Synthesized by Coprecipitation Method

1. Introduction:

Nanomaterials, which are often superior to their corresponding bulk material [1-4], have attracted much attention due to their crucial roles in future technological applications. It is well known that the properties of materials such as physical, optical and electronic ones are greatly dependent on their shapes, when their sizes were reduced to micrometer or nanometer scale [5]. So, many efforts have been devoted to the synthesis of materials with different shapes and sizes.

Spinel-type oxides (AB$_2$O$_4$) constitute one of the most interesting and important compounds, with applications in many different areas as magnetic materials, ceramics, catalysis and optical materials [6-10]. In the formula AB$_2$O$_4$, A indicates a divalent cation, B is trivalent cation. The AB$_2$O$_4$ spinel structure is characterized by two types of cation sites: tetrahedral for the divalent cation and octahedral for the trivalent cation. However, this structure is well-known for exhibiting cation exchange between tetrahedral and octahedral sites. The occupation of these two sites in the spinel-type oxides is affected by the combination and the nature of the two cations and depends strongly on the dopant content, annealing temperature and synthesis route [11-15]. The cation distribution can be characterized by the inversion parameter (y), which is defined as the fraction of the divalent cations in the octahedral sites or two times the fraction of trivalent cations in the tetrahedral sites. Taking into account the cation distribution, the general chemical formula of spinel can be written as $(A_{1-y}B_y) [A_yB_{2-y}]O_4$, where the round bracket and square bracket represent the tetrahedral and octahedral sites, respectively, and y denotes the
inversion parameter. Studies of cation distribution in spinels have attracted much attention because they may allow better understanding of the correlations between the structure and properties such as color, magnetic behavior, catalytic activity and optical properties etc., which are strongly dependent on the occupation of these two sites by metals [16-19].

Among the different materials investigated for use photocatalysts under solar light, spinel compounds are regarded as promising materials due their narrow direct band gap and high chemical stability [20]. It is known that the physical and chemical properties of spinel oxides are strongly affected by synthesis conditions and methods, as these influence chemical compositions, stoichiometry, point defect concentration and cation distribution. The spinel-type materials have attracted more attention from researchers. Due to their capabilities of accommodating different cations, they show various changes in electrical, magnetic and photocatalytic activity [21-25].

When an ion with incorrect valence enters the spinel structure, charged vacancies may form to maintain local charge neutrality. This is done by changing two divalent ions into a trivalent ion for every vacancy, but additional trivalent ion can also replace the divalent ion at the tetrahedral site. Both pathways increase the divalent and trivalent pair concentration at the octahedral site, thus enhancing electron hopping. In this chapter, we have studied the relationship between stoichiometry and electrical conductivity and photo-catalytic activity of dual-doped spinel oxide nanoparticles.
2. **Experimental**

2.1 **Synthesis of precursors**

High purity metal salts were used as starting materials. The required amount of metal salts was dissolved in distilled water and then added disodium carboxylate solution at appropriate pH. Quantities of the reactants were calculated according to the stoichiometry in the final product. The flow sheet diagram for dicarboxylate precursors and a subsequent conversion to substituted nanooxides is depicted in Fig.1.A.

2.1.1 **Cobalt aluminium tartarate tetra hydrate.**

\[(\text{NH}_4)_2[\text{CoAl}_2(\text{C}_4\text{H}_4\text{O}_6)_4(\text{OH})_2].4\text{H}_2\text{O}\]

This precursor was prepared by the coprecipitation method. Aluminium nitrate (20.00 g) and cobalt nitrate (10.00 g) were dissolved in a minimum amount of water and mixed with an aqueous solution of tartaric acid (40.00 g) in a 2:1:4 [Al(III) : Co(II) : Tartric acid] ratio. Ethanol was added to the final solution until a pink precipitate was formed. The pH was raised to 6 by adding NH\textsubscript{4}OH: Ethanol (1:1). After 24 hr at 4\textdegree C the pink precipitate was obtained. The solution was filtered. The precipitate was washed several times with cold distilled water. It was air dried at the ambient temperature. Yield = 40.582 g.

A similar procedure was used for the synthesis of 10 wt% doped cobalt aluminium tartarate precursor by taking the stoichiometric amount of zinc nitrate (0.406 g) and ferric nitrate (0.552 g) as dopant.

2.1.2 **Ammonium cobalt- molybdate hydroxide.**

\[(\text{NH}_4)\text{Co(OH)(MoO}_4)\]

This precursor was prepared by taking CoCl\textsubscript{2}.6H\textsubscript{2}O (0.1M) and ammonium heptamolybdate (0.1M) in double distilled water (100 ml). To this NH\textsubscript{4}OH solution
was added slowly with stirring, till a permanent precipitate was occurred. Added excess of ammonium hydroxide solution till precipitate get dissolved. This clear solution was stirred for two to three hours to get the final product. The light blue precipitate was filtered and washed with distilled water. It was air dried at the ambient temperature.

Yield = 20.037g.

A similar procedure was used for the synthesis of 10 wt.% doped ammonium cobalt- molybdate hydroxide precursor by taking stoichiometric amount of ferric nitrate (0.466 g) and ammonium metavanadate (0.135 g) as dopant.

2.1.3 Zinc-rhodium hydroxide dihydrate,

\[ \text{ZnRh}_2(\text{OH})_8\cdot2\text{H}_2\text{O} \]

A mixture of Zn(NO\textsubscript{3})\textsubscript{2}\cdot6\text{H}_2\text{O} (4.437 g), and RhCl\textsubscript{3}\cdot x\text{H}_2\text{O} (6.242 g) was dissolved in double distilled water (50 mL). Then these two solutions were mixed thoroughly on a magnetic stirrer, to this ammonium hydroxide solution (0.1M NH\textsubscript{4}OH) was added drop by drop until the precipitation is complete. The pH of the medium was maintained at ≤ 9. The brown precipitate i.e. ZnRh\textsubscript{2}(OH)\textsubscript{8}\cdot2\text{H}_2\text{O} was then digested at 90\degree C for one hour. The solution was filtered and washed with a dilute ammonium hydroxide solution to obtain material free of chloride ion. (A silver nitrate solution was used to test the absence of chloride ion). The precipitate was then dried in an oven in air at 100\degree C for 24 h and then ground with the help of agate mortar. The obtained powder sample was restored in a desiccator. Yield = 4.451 g.

A similar procedure was used for the synthesis of 10 wt% doped Zinc-rhodium hydroxide precursor by taking the stoichiometric amount of bismuth nitrate (0.351 g) and dysprosium nitrate (0.330 g) as dopant.
2.1.4 **Zinc-iron tartarate tetra hydrate.**

\[ \text{ZnFe}_2(\text{C}_4\text{H}_4\text{O}_6)_{4.4}\text{H}_2\text{O} \]

A mixture of \( \text{Zn(NO}_3\text{)}_{2.6}\text{H}_2\text{O} \) (7.404 g), and \( \text{FeSO}_4.7\text{H}_2\text{O} \) (13.838 g) was dissolved in double distilled water (50 mL). The pH of the medium was adjusted to a low enough value (pH < 6), so that hydroxide precipitate does not form. To this disodium tartarate solution (22.905 g dissolved in minimum distilled water) was added slowly with constant stirring till a permanent precipitate was occurred. Acetone was added in equal amount to get more homogeneous, stoichiometric fine grained powders. The precipitate was filtered and washed with cold distilled water and then with acetone. It was air dried at the ambient temperature. Yield = 14.476 g.

A similar procedure was used for the synthesis of 10 wt% doped zinc-iron tartarateprecursor by taking the stoichiometric amount of manganese chloride (0.210 g) and copper nitrate (0.250 g) as dopant.

2.1.5 **Praseodymium-vanadium oxalate hydrate**

\[ \text{PrVO(C}_2\text{O}_4)_{2.5}\text{H}_2\text{O} \]

This precursor was prepared by taking \( \text{NH}_4\text{VO}_4 \) (2.143 g), and \( \text{Pr(NO}_3\text{)}_{3.6}\text{H}_2\text{O} \) (7.472 g), in double distilled water (50 mL). Ammonium metavanadate first dissolved in hot distilled water. The pH of the medium was adjusted by adding oxalic acid. Then the solution of praseodymium nitrate was added in calculated amount. The solution was stirred vigorously with a magnetic stirrer. Stirring continued till a permanent precipitate occurred (after one hour). The resultant precipitate of \( \text{PrVO(C}_2\text{O}_4)_{2.5}\text{H}_2\text{O} \) was yellow in color. The solution was filtered. The filtrate was checked for \( \text{Pr}^{3+} \) ions whose absence ensured complete precipitation. The precipitate was washed with cold distilled water and then with acetone to speed up the drying. It was air dried at the ambient temperature Yield = 11.034 g.
A similar procedure was used for the synthesis of 10 wt.% doped praseodymium-vanadium oxalate precursor by taking the stoichiometric amount of gadolinium nitrate (0.435 g) and ruthenium chloride (0.200 g) as dopant.

2.2 Synthesis of nanocrystalline undoped and dual doped spinel oxides

The above precursors were decomposed and calcined slowly at 700°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 the sample was removed at room temperature. The obtainable undoped spinels such as CoAl₂O₄, CoMoO₄, ZnRh₂O₄, ZnFeO₄, PrVO₄ and their respective dual doped spinel nano oxides such as Co₀.₉₅₃Zn₀.₀₄₇Al₁.₉₅Fe₀.₀₅O₄, Co₀.₉₅₇Fe₀.₀₄₃Mo₀.₉₅₄V₀.₀₄₆O₄, Zn₀.₉₄₉Bi₀.₀₅₁Rh₁.₉₅₁Dy₀.₀₄₉O₄, Zn₀.₉₃₃Cu₀.₀₄₇Fe₁.₉₄₅Mn₀.₀₆₅O₄ and Pr₀.₉₅₂Gd₀.₀₄₈V₀.₉₅₆Ru₀.₀₄₄O₄ were restored in a desiccator.

2.3. Physical analysis

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

2.4. Photocatalytic activity measurements

The photodegradation activity of dual doped spinel oxides was measured using Victoria blue-B and Brilliant yellow water solution. The experimental detail for
photocatalytic activity measurement is explained in Chapter II. The initial concentration of Victoria blue-B (100 mg/l) or Brilliant yellow (20mg/l) in a reaction vessel was fixed with a catalyst loading of 50mg. Before irradiation, the suspensions were initially sonicate for 2 min., and then stirred for 20 min. in the dark to reach in adsorption-desorption equilibrium. Sun light was used between 11.30 a.m. to 3.00 p.m. During irradiation using sunlight, stirring was maintained and, at regular time intervals, dye samples were withdrawn and centrifuged to separate spinel oxide particles. The extent of these dyes degradation was monitored by measuring the absorbance at 580nm and 402nm (λmax) for Victoria blue-B and Brilliant yellow respectively, using UV-vis-spectrophotometer.

3. Results and discussion

3.1 Characterisation of precursor

A quantitative tartarate/oxalate coprecipitates are obtained from the started high concentrated metal salt solution with slow addition of saturated disodium dicarboxylate/hydroxide solution in stoichiometric proportion in water- acetone mixture. Here, the addition of acetone not only ensure a high yield, but also influences more homogeneous and fine-grained powders. The precipitation form is also based on tartarate/oxalate or hydroxide, provided the pH is maintained at a low enough value (pH≤6), so that the hydroxide precipitate do not formed. The solution mixture ware stirred continuously with a magnetic stirrer and digested it at 60°C for complete precipitation of precursor. Then it was cool and filtered through whatmann No.41 filter paper. The precipitate was washed several times with distilled water and then distilled acetone. The obtained precipitate was dried for 2hr at 100°C and then stored in desiccator.
The elemental analysis of tartarate/oxalate and hydroxide coprecipitate such as cobalt-aluminium tartarate tetrahydrate, \((\text{NH}_4)_2[\text{CoAl}_2(\text{C}_4\text{H}_4\text{O}_6)_4(\text{OH})_2].4\text{H}_2\text{O}\); cobalt-molybdate hydroxide, \((\text{NH}_4)\text{Co(OH})(\text{MoO}_4)\); zinc-rhodium hydroxide dihydrate, \(\text{ZnRh}_2(\text{OH})_8.2\text{H}_2\text{O}\); zinc-iron tartarate tetrahydrate, \(\text{ZnFe}_2(\text{C}_4\text{H}_4\text{O}_6)_4.4\text{H}_2\text{O}\); and praseodymium oxovanadium oxalate dihydrate, \(\text{PrVO}(\text{C}_2\text{O}_4)_2.5.2\text{H}_2\text{O}\) are presented in Table I and it is in good agreement with the required values. The thermal analysis confirmed the presence of water of hydration of these precursors. The X-ray fluorescence spectroscopy (XRF) analysis further confirms all cations were present in a perfect cationic ratio in the precursors (Table I).

Fig. 2 displays an infrared spectrum of tartarate/oxalate and hydroxide precursor. The band at 3444 cm\(^{-1}\) is assigned to the hydroxide group and the intense band at 1599 cm\(^{-1}\) due to \(\nu_{\text{asy}}\) (C = O) and band at 1491 cm\(^{-1}\) and 1390 cm\(^{-1}\) due \(\nu_{\text{sy}}\) (C-O) (see Table II). These values indicate the presence of the coordinated carboxylate group [26]. The infrared spectral analysis showed bidentate linkage to be more favorable for tartarate/oxalate precursors on the basis of the difference between \(\nu_{\text{asy}}\) and \(\nu_{\text{sy}}\) (C-O) stretching frequencies. The infrared spectra in the range 1070-997 cm\(^{-1}\) suggest the free \(-\text{OH}\) group to metal in solid state [27-29]. Other bands in Table II are all combination bands may be assigned to different normal modes of vibrations of the carboxylate group [26]. The \(\nu_{\text{M-O}}\) vibrations has been identified for these precursors at 553 cm\(^{-1}\), which suggested a six coordination environment for the metal ions in the complex [30,31]. The water molecules present in the precursors constitute a very small amount of free and absorbed as well as the remained on the surface of the precursors. The chain like polymeric octahedral structure has been assigned to these precursors.
While, the infrared spectra of hydroxide precursors such as NH₄Co(OH)(MoO₄) and ZnRh₂(OH)₈.2H₂O were recorded in the 4000-400 cm⁻¹ range. The broad band at 3362 and 1610 cm⁻¹ are attributed to the stretching and bending vibrations of the O-H bond, respectively [32]. The middle bands at 1413 cm⁻¹ and 1273 cm⁻¹ are assigned respectively to υ_NH₄⁺ and υ_N-OH bands for NH₄Co(OH)(MoO₄) precursor. It is reported that there are two types fundamental absorption bands at 920 and 866 cm⁻¹ due to vibration of (MoO₄)²⁻ group [26].

The thermal analysis (TGA and DTA) results are shown in Fig.3. The TGA traces of all samples display a multistep mass loss in static air atmosphere. There are two main steps in the thermal decomposition reaction observed in these precursors, (i) dehydration and (ii) oxidative decomposition of dicarboxylate or hydroxide. As depicted in Fig.3, the TGA curve for the first step of little mass loss observed started from room temperature and went up to 180°C, which is related to the loss of adsorbed water molecules (Table III). A broad endothermic peak in the DTA curve at around 100°C indicated to the dehydration of precursor. In the second step of TGA curve showed mass loss at 180-700°C corresponding to the formation of respective metaloxides. The observed mass losses are reasonable with the calculate value (see Table III). The strong and broad exothermic peak found in the DTA curve at ~340°C indicating that the thermal events can primarily associate with the burnout of organic species or removal of hydroxide species in the precursor powder.

On the basis of TGA and DTA studies, the following tentative scheme is proposed for the thermal decomposition of precursor in static air as

a) For Co-Al tartarate

\[
\text{(NH}_4\text{)}_2 \text{[CoAl}_2\text{(C}_4\text{H}_6\text{O}_6\text{)}_4\text{(OH)}_2\text{].4H}_2\text{O} \xrightarrow{25-115^\circ C} \text{(NH}_4\text{)}_2 \text{[CoAl}_2\text{(C}_4\text{H}_6\text{O}_6\text{)}_4\text{(OH)}_2\text{]} + 4\text{H}_2\text{O}
\]
(NH₄)₂[CoAl₂(C₄H₄O₄)(OH)₂]  115-245°C  [CoAl₂(C₄H₄O₄)] + NH₃↑ + H₂O

[CoAl₂(C₄H₄O₄)₄]  245-800°C  CoAl₂O₄ + CO₂↑ + CH₄↑ + CO↑

b) For Co–Mo hydroxide

(NH₄)Co(OH)(MoO₄)  30–650°C  CoMoO₄ + NH₃↑ + H₂O

c) For Zn-Rh hydroxide

ZnRh₂(OH)₈·2H₂O  30–125°C  ZnRh₂(OH)₈ + 2H₂O

ZnRh₂(OH)₈  125–750°C  ZnRh₂O₄ + 4H₂O

d) For Zn–Fe tartarate

ZnFe₂(C₄H₄O₄)₄·4H₂O  30-150°C  ZnFe₂(C₄H₄O₄)₄ + 4H₂O

ZnFe₂(C₄H₄O₄)₄  150-650°C  ZnFe₂O₄ + 2C₂H₂↑ + 3CO₂↑ + 2C₂H₄↑ + 3O₂↑

e) For Pr–V oxalate

PrVO (C₂O₄)₂.₅ ·2H₂O  30–110°C  PrVO (C₂O₄)₂.₅ + 2H₂O

PrVO (C₂O₄)₂.₅  110–650°C  PrVO₄ + 2CO₂↑↑ + 3CO↑

3.2 Characterization of dual doped spinel oxides

3.2.1 Compositional analysis

The above tartarate / oxalate or hydroxide precursors are calcined in normal (static) air at 600°C. To improve the degree of reaction and to avoid the presence of secondary phases, a special process was applied consisting of double calcinations at same temperature for 2h under normal air atmosphere with an intermediate grinding. The composition undoped and dual doped spinel oxides such as CoAl₂O₄, Co₀.₉₅₃Zn₀.₀₄₇Al₁.₉₅Fe₀.₀₅O₄; CoMoO₄, Co₀.₉₅₇Fe₀.₀₄₃Mo₀.₉₅₄V₀.₀₄₆O₄; ZnRh₂O₄, Zn₀.₉₄₀Bi₀.₀₅₁Rh₁.₉₅Dy₀.₀₄₉O₄; ZnFe₂O₄, Zn₀.₉₅₃Cu₀.₀₄₇Fe₁.₉₄₀Mn₀.₀₆₄O₄; PrVO₄, Pr₀.₉₅₂Gd₀.₀₄₈V₀.₉₄₀Ru₀.₀₄₄O₄ were determined by XRF and EDAX analysis. The required and observed compositions are summarized in Table IV. They are found to
be ±0.5 wt.% of nominated values. The proportion of ingredient elements showed that the weight proportions are correct in the final product. Energy dispersive X-ray analysis (EDAX) spectra (Fig.4 & 5) in all undoped and dual doped spinel oxides confirmed the dopant peak heights relative to the element varied in the correct sense according to the concentration of dopant expected by the nominal composition. Within each composition, the dopant peak heights for each sample are reasonably consistent. The elemental composition analysis at several spots is uniform, which is indicative of a highly homogeneous material (see Fig.4 and 5). This is due to fact that all the cations are uniformly mixed.

3.2.2 X-ray diffraction studies

The powder X-ray diffraction patterns of undoped and dual doped spinel oxides are depicted in Fig.6. Crystalline nature can be derived from the appearance of sharp diffraction peak in the XRD pattern of these samples prepared by the precursor method, which indicate that all passes single spinel phased. The observed d-spacing values and relative intensities (Table V) are compared with those reported in literature [33-37]. The lattice parameter of each undoped and doped spinel oxide is then calculated and is shown in Table VI. All XRD peaks are well assigned to the cubic structure for CoAl₂O₄, Co₀.₉₅₃Zn₀.₀₄₇Al₁.₉₅₃Fe₀.₀₄₇O₄; ZnRh₂O₄, Zn₀.₉₄₉Bi₀.₀₅₁Rh₁.₉₅₁Dy₀.₀₄₉O₄; ZnFe₂O₄, Zn₀.₉₅₃Cu₀.₀₄₇Fe₁.₉₄₄Mn₀.₀₆O₄, while monoclinic structure for CoMoO₄, Co₀.₀₉₅₇Fe₀.₀₄₃M₀.₉₅₄V₀.₀₄₆O₄ and tetragonal structure for PrVO₄, Pr₀.₉₅₂Gd₀.₀₄₈V₀.₉₅₆Ru₀.₀₄₄O₄ samples respectively. From Table VI, it can be seen that the lattice constant slightly increases with the dual dopants as compared to undoped spinel oxides. This can be explained based on the relative sizes of ionic radii of different dopant ions. The replacement of larger dopant cations for small host cations in the prepared spinel
oxides causes are increases in lattice parameter. Obviously, there is a basic correlation between the lattice parameter value and the anion-cation distance for a particular site (i.e. A or B site) in the spinel structure [38, 39].

The crystallite size of the spinels can be estimated from the Scherrer equation [40]. \( D = 0.89*\lambda/\beta \cdot \cos \theta \), where \( D \) is the average grain size, \( \lambda \) is the X-ray wavelength (0.15405 nm), \( \theta \) and \( \beta \) are the diffraction angle and the full width of half maxima of an observed peak, respectively. The strongest 3-4 peaks are used to calculate the mean crystalline size \( <D> \cdot \text{x-ray} \) for all samples. The estimated mean crystallite size is depicted in Table VI. These values are in the range of 15.86 to 62.50 nm for all samples, indicating the nanocrystalline nature.

From mean crystallite size, the total surface area can be calculated [41] by using relation \( d_{VA} = 6 \cdot V/A \), where \( d_{VA} \) is mean crystallite diameter \( <D> \cdot \text{x-ray} \) in nm, \( V \) is the volume of crystallite, which determine from lattice parameter and \( A \) is the total surface area. Then, calculate the surface area \( A \) in terms of \( \text{m}^2/\text{gm} \); these values are also indicated in Table VI.

3.2.3 Particulate properties

Density plays a key role in controlling the properties of polycrystalline spinel oxides. Using the values of lattice parameters, we calculated the X-ray density (\( D_x \)) and porosity (\( P \)) from relation, which is given in chapter II. The results of the particulate properties like X-ray density (\( D_x \)) measured apparent density (\( D \)) and porosity (\( P \)) of all the samples are given in Table VI. It is noticed that X-ray densities, \( D_x \) are higher than the apparent density (\( D \)). This is attributed to the existence of pores, which depends on the sintering conditions. As the pores are basically spaces between particles, it is considered that the shape of pores is influenced by the shape of the particles [42]. This is supported by scanning electron micrograph (SEM).
Morphology of undoped and dual doped spinel oxides is studied by SEM and which are given in Fig. 7 and 8. The grain shape of CoAl₂O₄ is spherical in shape, but the degree of agglomeration is high, while in doped compound showed an irregular plateless with small grain on it (see Fig. 7 (a) and (b)). The large and small rectangular like grains are seen for CoMoO₄ spinel and in contrast to this, the grain of Co₀.₉₅⁷Fe₀.₀₄₃Mo₀.₉₅₄V₀.₀₄₅O₄ had little agglomeration and consist of spherical grains (Fig. 7 (c) and (d)).

As can be seen in Fig. 7 (e) and (f) respectively, for ZnRh₂O₄ and Zn₀.₉₄₉Bi₀.₀₅₁Rh₁.₉₅₁Dy₀.₀₄₉O₄, the particles are more or less spherical but the degree of agglomeration is high. Similar natures of grains are seen for ZnFe₂O₄ and Zn₀.₉₅₃Cu₀.₀₄₇Fe₁.₉₄₀Mn₀.₀₆O₄ samples (see Fig. 8(a) and (b)). While in Fig. 8(c) and (d), the particle are square shape with large and small shapes for PrVO₄ and Pr₀.₉₅₂Gd₀.₀₄₈V₀.₉₅₆Ru₀.₀₄₄O₄ compounds. All the undoped and dual doped spinel oxides exhibit the average grain size are given in Table VI and it is found in the range of 29.96 to 68.07 nm.

### 3.2.4 Infrared spectral studies

The infrared spectra of undoped and dual doped spinel oxides have two strong and somewhat broad band at ν₁ ~ 657 cm⁻¹, ν₂ ~ 554 cm⁻¹, ν₃ ~ 484 cm⁻¹ and are given in Table VI. The broadening is due to the statistical distribution of cations over A and B site of spinel structure. It is well known that CoAl₂O₄, ZnRh₂O₄ and ZnFe₂O₄ and its corresponding doped spinel have normal spinel structure.

According to group theory spinels should exhibit three normal vibrational modes in the mid IR region [43]. A breakdown of the IR selection rules can occur due to various factors which can subsequently lead to an increase in the number of IR modes. According to Wang et.al.[44], for normal spinel this vibration occurs at
666cm\(^{-1}\), 554cm\(^{-1}\) and 504cm\(^{-1}\) spectral regions. On the other hand, typical bands of inverse spinel, having tetrahedrally coordinated metal ions are at 626 and 559 cm\(^{-1}\) [45]. The absorption at ~670 cm\(^{-1}\) is generally assigned to the M-O stretching vibration of the MO\(_6\) octahedral [43, 45]. On the other hand absorption band at 626 cm\(^{-1}\) point out the tetrahedrally coordinated metal ion, which is present in the inverse spinels. Bands at ~554 cm\(^{-1}\) also to be assigned to M-O stretching vibration of MO\(_6\) octahedral groups [43, 46], but also to the M-O stretching vibration the MO\(_4\) tetrahedra[45, 47]. The lower frequency band (\(v_3\)) at ~484 cm\(^{-1}\) is attributed to the M-O stretching vibration of the MO\(_4\) tetrahedral [46, 47], or to combined vibrations of both cations in tetrahedral or octahedral sites [48-51]. Also, the band at \(v_3\) representing the B-site (octahedral) lies ~450cm\(^{-1}\). The band in the range of 560-550cm\(^{-1}\) (\(v_2\)) and 484-437cm\(^{-1}\)(\(v_3\)) gave no specific information because it is typical for both, the normal and inverse spinel in a very narrow wavelength interval and literature offers no clear recipe for its attribution. As we can see from Table VI, there is slight deviations in the positions of the peak \(v_1\), \(v_2\) and \(v_3\), are mainly due to the factors like method of preparation, grain size and density [52]. Therefore, from infrared spectral data CoAl\(_2\)O\(_4\), ZnRh\(_2\)O\(_4\), ZnFe\(_2\)O\(_4\) and their dual doped spinels shows to be normal spinel structure. The splitting of \(v_2\) and \(v_3\) into shoulder has not been observed in present compounds, which also confirms the absence of excessive M\(^{2+}\) ions at the octahedral site (i.e. B-site) of spinel structure.

Infrared spectra were used to examine the bonding nature in the prepared CoMoO\(_4\) and its dual doped compound. Their bandpositions are listed in the Table VI. As we can see in the table that presence of three major band at 910,685 and 464cm\(^{-1}\). The band observed at ~910cm\(^{-1}\) corresponds to the vibrational modes of distorted MoO\(_4\) present in CoMoO\(_4\) [26]. The band at 685 cm\(^{-1}\) corresponds to the vibrational
mode of Mo-O in the CoMoO$_4$, and the band at 464 cm$^{-1}$ represents vibrations due the Co and Mo building blocks of CoMoO$_4$ \cite{53,54}.

Infrared spectral data of PrVO$_4$ and Pr$_{0.952}$Gd$_{0.048}$V$_{0.956}$Ru$_{0.044}$O$_4$ are depicted in Table VI. There are three major bands observed at 1050, 825 and 663 cm$^{-1}$ respectively corresponds to the vibrations due mode of V=O, O-V-O bending and V-O in the distorted spinel structure.

3.2.5 **Electrical conductivity studies**

Temperature dependent d.c. electrical conductivity measured on undoped and dual doped spinel oxide such as CoAl$_2$O$_4$, Co$_{0.953}$Zn$_{0.047}$Al$_{1.95}$Fe$_{0.05}$O$_4$; CoMoO$_4$, Co$_{0.957}$Fe$_{0.043}$Mn$_{0.954}$V$_{0.046}$O$_4$, ZnRh$_2$O$_4$, Zn$_{0.949}$Bi$_{0.051}$Rh$_{1.951}$Dy$_{0.049}$O$_4$; ZnFe$_2$O$_4$, Zn$_{0.953}$Cu$_{0.047}$Fe$_{1.940}$Mn$_{0.06}$O$_4$, PrVO$_4$, Pr$_{0.952}$Gd$_{0.048}$V$_{0.956}$Ru$_{0.044}$O$_4$ in the temperature range 322–862 K is shown in Fig. 9. Here log $\sigma$ plotted versus $10^3/T$ shows an initial decrease in electrical conductivity in the temperature range 30 to 130°C. The $\sigma$ values are then increased showing two distinct slope with a ‘break’ for all spinel compounds except PrVO$_4$ and its doped spinel oxides. The initial decrease in conductivity corresponds to desorption of adsorbed water molecules on particle surface, usually adsorbed water molecules behave as an electron donor. Fig. 9 also shows that, there are two temperature region (Region A and B) with different activation energy, the temperature at which the break occur was found to be about 600K i.e. transition temperature Tc (see Table VII). This discontinuity can be attributed to a phase transition from extrinsic to intrinsic semiconductor. The conductivity in the region A (322 – 600 K) corresponds to lattice defect present and the smaller mobility of the defects, while conductivity at high temperature region B (640 – 862 K) to a thermally activated mobility of the charge carriers \cite{55}. The explanation as follows: Since, spinel system contains a number of defects in the form of divalent, trivalent and
oxygen vacancies, these produce local deformation in the system to the local
displacement in the direction of the local electrical field resulted in due to the electron
hopping. Thus, in region A (from 322 to 600K) a number of electron together with the
defects present in the spinel system form small polorons. So in addition to electron
hopping, the hopping of the small polorons between adjacent sites, i.e. tetrahedral and
/or octahedral sites occupied by the divalent and trivalent ions, also contributes to the
conductivity i.e. extrinsic type semiconductor. Also, in spinel system the charge
compensation can take place by the creation of oxygen vacancies. Therefore, in region
B(640-862K), the electrical conductivity is believed to be increased with increase in
temperature mainly due to the thermally activated mobility of electrons and that of the
small polar ions, the hopping of which is enhanced by rise in temperature [56,57] i.e.
intrinsic type semiconductor. For PrVO₄ and its doped spinel oxide have a thermally
activated charge carriers, i.e. hopping of mobility of charges from \( V^{5+} \rightarrow V^{4+} \) and
vice-versa.

From the Arrhenius plots (Fig.9) the energy of activation (Ea) of carriers
(electrons and small polorons) was calculated by the relation [58, 59]:
\[
\sigma = \sigma_0 \exp(-\frac{E_a}{K T}),
\]
where Ea is activation energy, \( \sigma_0 \) is temperature independent
constant, K is Boltzmann’s constant and T is the absolute temperature. The two
activation energies (Ea) are calculated from plot of \( \log{\sigma} \) vs \( T^{-1} \), a straight line exhibit
at region A and B, the slope of which was used to calculate the activation energy as
shown in Table VII. It is noted that the activation energy Ea in region B is higher
than in the region A for all undoped spinel oxides. In contrast to this, on dual doping
of spinel oxides, the activation energy Ea in region B is lower than in the region A
and also undoped spinel oxides. For undoped spinel oxides, the electrical conductivity
is due to the electron hopping in sub lattice between \( M^{2+} \rightarrow M^{3+} \) or \( M^{3+} \rightarrow M^{4+} \).
(as in case of ZnRh$_2$O$_4$ spinel) ion at the octahedral site and results increasing in activation energy, $E_a$ in the region B.

While in the present study, $M^{3+}$ ions are partially replaced by dopant ions at both octahedral B-site and tetrahedral A-site in spinel compounds (i.e. called dual doped spinel oxides). The dopant ions in the present study such as Co$^{2+}$, Rh$^{3+}$, Fe$^{3+}$, Dy$^{3+}$, Mn$^{3+}$, Ru$^{3+}$, Pr$^{3+}$, Gd$^{3+}$ ions etc. that are known to have strong preference to the octahedral B-site; while Al$^{3+}$, Mo$^{3+}$, Zn$^{2+}$, V$^{5+}$, Mo$^{5+}$, Bi$^{3+}$, Cu$^{2+}$, Ru$^{4+}$ occupy at tetrahedral A-site. They are all depends on the crystal field stabilization energies of the metal ion [60-62]. The dopant ions present at tetrahedral A-sites, which have no contribution in conductivity therefore conductivity decreases [63]. While dopant ion replace the $M^{3+}$ ions at octahedral B-site, which may impede the conduction process. This is because in the spinel system, the dopant substitution of $M^{3+}$ ions at octahedral B-site, form small polarons could approach each other and their polarization overlapped. This could results in reducing the required hopping energy [64] and a decrease in the activation energy $E_a$ with dopant contents could have been observed contrary in our result. Another possible explanation for observed decrease in activation energy (Ea) is based on changes of the ionic distances in the spinel crystal structure. Also, a decrease in lattice volume manifests as a corresponding decrease in the inter-ionic distances, and consequently, as reduction in the barrier height encountered by hopping charge carriers[65]. Therefore for dual doped spinel oxides have lower activation energies, $E_a$ as compared to undoped spinel oxides at high temperature region B.

3.2.6 Thermoelectric power measurements

The thermoelectric power measurement for undoped and dual doped spinel oxides showed n-type semiconductor (Fig.10 (a) and (b)). The initial decrease of
negative carrier (up to 420K) might be due to desorption of the adsorbed water molecules on the particle surface. For temperature above 420K, its magnitude increases as the temperature increases, which corresponding to conduction mechanism via oxygen vacancies lead to an electronic conduction of n-type charge carriers for all spinel oxides (see Table VII). It is well known that conductivity (σ) and thermoelectrical powder (µ) are inversely related as a function of carrier concentration, i.e. higher carrier concentration are associated with lower conductivity and smaller thermoelectrical power [66,68]. In contrast, higher mobility leads to larger values for both σ and (µ) [69, 70]. The positive and negative effects of increases carrier mobility and carrier concentration respectively, on (µ) might be balanced in general, and thus, PrVO₄ and Pr₀.952Gd₀.048V₀.956Ru₀.044O₄ displayed the highest thermoelectric power (µ) value.

### 3.2.7 Dielectric studies

Variation of dielectric constant (ε’) and dielectric loss (tan δ) for different frequencies at room temperature is shown in Figs. 11 and 12 respectively for undoped and dual doped spinel oxides. The dielectric constant decreases with increase in frequency. It shows dispersion behavior in lower frequency region and attains a constant value at higher frequencies (Fig.11). Dielectric dispersion in undoped and doped spinel oxides can be explained on the basis of space charge polarization, which is a result of the presence of higher conductivity phases (grains) in the insulation matter (grain boundaries) of a dielectric causing localized accumulation of charges under the influence of an electric field [71,72]. The decrease of dielectric constant with frequency is due to Maxwell-Wagner type interfacial polarization in agreement with Koop’s phenomenological theory. The polarization mechanism in spinel oxides is similar to the conduction process. Due to the presence of M³⁺ and M²⁺ metal ions,
the spinel materials are referred as a dipolar. Orientation polarization arises due to the rotational displacement of dipoles.

The undoped and doped spinel oxides, at low frequency, rotation of \(M^{2+}\) to \(M^{3+}\) dipoles may be visualized as the exchange of electrons between the ions, so that the dipoles align themselves in response to the alternating field gives the maximum polarization. The polarization decreases (i.e. dielectric loss) with increase in frequency and reaches a constant value (Fig.12) due to the fact that beyond a certain frequency of external field the electron exchange between \(M^{3+}\) and \(M^{2+}\) metal ions on octahedral site cannot follow the alternating field [73]. In dual doped spinel oxides, the dopants like \(\text{Co}^{3+}\), \(\text{Fe}^{3+}\), \(\text{Dy}^{3+}\), \(\text{Mn}^{3+}\), and \(\text{Gd}^{3+}\) etc. ions occupy octahedral sites due to its larger ionic radius. This reduces the concentration of \(M^{3+}\) ions at octahedral B-site, which play a dominant role in dielectric polarization. Due to the decrease in concentration of \(M^{3+}\) ions, electron transfer between \(M^{2+}\) to \(M^{3+}\) will be slowed down i.e. the polarization decreases. Accordingly, dielectric constant decreases with dopant content [74]. The variation in \((\tan \delta)\) with frequency for all undoped and doped spinel oxides shows a similar kind of dispersion (see Fig.12). At lower frequencies, \(\tan \delta\) is larger and then decreases with increasing frequency. The high value of \(\tan \delta\) at lower frequencies corresponds to high value of resistivity due to grains boundaries. Hence, more energy required for electron exchange between \(M^{2+}\) and \(M^{3+}\) ions at B-site, resulting in high value of energy loss. In the high frequency range, small amount of energy is required for electron transfer between \(M^{2+}\) to \(M^{3+}\) ions resulting in small energy loss and low value of respectively [75]. In other word, dielectric loss \((\tan \delta)\) is directly proportional to conductivity. The relation between dielectric loss \((\tan \delta)\) and electrical conductivity is given by following relation [74].

\[
\tan \delta = \frac{1}{2 \Pi f R C}
\]
Where $\delta$ is the loss angle, $f$ is the frequency, $R$ is equivalent series resistance and its inverse is the conductivity, and $C$ is the equivalent series capacitance.

3.2.8 **Photocatalytic studies**

Photocatalytic properties of undoped and dual doped spinel oxides nanoparticles have been emerged to be great interest due to their potential catalytic performance and low cost nature. Light absorption is an important factor for the photocatalytic performance and evaluation of the photocatalytic activity of the materials. Therefore, the electronic structure of the materials as well as the migration of the light – induced electrons and holes should be clarified [76,77].

3.2.8.1 **Band gap measurement**

Fig.13. Show the UV-vis. diffuse reflectance spectra (DRS) of undoped and dual doped spinel oxides to study their photo absorption ability. These samples display the photo absorption properties at the region of visible light with the wavelength longer than 710nm. This can be ascribed to the band gap transition of the samples. The band gaps of samples can be estimated by the equation $E_g=1240/\lambda$ [78], in which $E_g$ is band gap energy of photocatalyst in electron volts, and $\lambda$ is absorption edge wavelength in nanometers. Band gap energy thus obtained for undoped and dual doped spinel oxides are depicted in Table VIII. It can also be observed from Fig.13 that an inflexion appear in each DRS curve. The inflexion wavelengths obtained from Fig.13 are given in Table VIII for undoped and dual doped spinel oxides. It is noticed that the dual doped spinel oxides showed a remarkable absorption band shift toward the longer wavelength region which indicates a decrease of the band gap energy ($E_g$) (see Table VIII). This may be due to a defect (such as oxygen vacancies) in the
synthesized photocatalyst[79]. This electron-hole may improve photodegradation, but most of them are trapped by sub-surface recombination [80].

3.2.8.1 Photodegradation studies on Victoria blue–B and Brilliant yellow solution

(a) Preliminary experiments

The influence of solar light on color removal of dyes was investigated. One experiment was performed in the absence of any catalyst under direct sunlight. No significant change in color of Victoria blue-B or Brilliant yellow is observed even after 3h. This reveals that this dye does not undergo solar photolysis. These dyes are degraded completely in 3h in the presence of catalyst (spinel oxides) and solar light. Therefore we have decided to study the effect of various parameter on photodegradation of these dyes.

(b) Effect of initial dye concentration

The effect of dye concentration was also observed by taking different concentration of Victoria blue-B and Brilliant yellow by taking 50mg amount for spinel oxides under sun light. The results are represented in Fig. 14(a) and (b) respectively for both the dyes. The rate of photocatalytic degradation of these dyes was found to increase on increasing the concentration up to Victoria blue-B = 100mg/L and Brilliant yellow = 20mg/L. It may be due to the fact that as the concentration of dye was increased, more dye molecules were available for excitation and consecutive energy transfer. As a result, increase in the rate of percent degradation was observed. The rate of photocatalytic degradation was found to decrease with further increase in the concentration of the dyes. So at high concentration, it will not permit the desired light to reach the spinel oxides particles. Thus, decreasing the percent degradation of the dyes.
(c) **Effect of amount of spinel oxide**

The amount of undoped spinel oxides may also affect the process of dye degradation and hence different amounts of spinel oxides were used under sun light. Here we kept the dye concentration constant i.e. 100mg/L for Victoria blue-B and 20mg/L for Brilliant yellow. It was observed that initially, the percent of degradation of Victoria blue-B and brilliant yellow increases with an increase in the amount of spinel oxides, but it becomes decreases after a certain amount of spinel oxides (see Fig. 14(b) and (b')). This may be attributed to the fact that as the amount of spinel oxide is increased, the exposed surface area of spinel oxide also increases. After a certain limit, there was no increase in the exposed surface area of the photocatalyst, even if the amount of spinel oxide was further increased. Above this point, any increase in the amount of spinel has negligible effect on the rate of percent degradation of dyes.

(d) **Effect of pH on dye degradation**

The influence of initial pH value from 2 to 10 on the percent degradation of Victoria blue-B (100mg/L) and Brilliant yellow (20mg/L) at constant amount of spinel oxides (50mg) under sun light is shown in Fig.14(c) and (c'). It has observed that the percent degradation increases with increase in pH up to 7.5 and then decreases for Victoria blue-B dye, while the percent decreases from pH=2.5 for Brilliant yellow dye. From it is concluded that the photocatalytic reaction occurs not only on the catalyst surfaces but also in the close vicinity of the spinel oxide surface. The acid base property of the spinel oxide surface can have considerable implications upon their photocatalytic activity. The spinel oxides surface is negatively charged by means of adsorbed OH\(^{-}\) ions. The presence of large quantities OH\(^{-}\) ions on the particle surfaces favors the formation of hydroxyl radical, which is the principal oxidizing
species responsible for the dye degradation process. The production of hydroxyl radicals in an acidic medium (i.e. at pH=2.5) is different from what occurs in a basic medium (pH=7.5). In an acidic medium, photogenerated holes react with water molecules to produce hydroxyl radicals.

(c) Effect of contact time

After confirmed the effect of dye concentration, amount of photocatalyst and pH, we have decided to study the photodegradation of dye with contact time. The photocatalytic activity of undoped and dual doped spinel oxides (50mg) was investigated by measuring the degradation of Victoria blue-B (10mg/0.1L) and Brilliant yellow (20mg/L) in aqueous solution at pH = 7.5 and pH = 2.5, respectively. Fig. 15 (a) depicts the percent degradation of undoped and dual doped spinel oxides at different time intervals. The photocatalytic activity of ZnFe$_2$O$_4$ and its doped compound such as Zn$_{0.953}$Cu$_{0.047}$Fe$_{1.940}$Mn$_{0.06}$O$_4$ is obviously higher than that of other undoped and dual doped spinel oxides. It seems that in zinc ferrite, the Fe$^{2+}$ defects at the octahedral site could initiate recombination. The results of percent degradation are depicted in Table VIII. As it can be noticed that the percent degradation of both the dyes showed higher photocatalytic activity for dual doped spinel oxides as compared to undoped spinel oxides. It is known that ionic defect can form donor and acceptor level in the electronic structure of spinels [81,82] and these levels can act as recombination center for effective charge carriers [83]. On the other hand, it has been reported that various point defects, for example oxygen vacancies together with oxygen interstitials, can improve charge separation in some spinel oxides, thus increasing photo activity [84]. On doping into spinel oxide can introduce new electronic state in spinel to form an addition interband site [85]. Therefore, on doping of different cations at A- and B-sites of spinel, increases the number of
photogenerated electrons and holes to participate in the photocatalytic reaction, which results in high photocatalytic activity.

From Table VIII, we can also observed that the percent degradation of Victoria blue-B in water on all undoped and dual doped spinel oxide is obvious higher than that of Brilliant yellow in water. This may be due to high basic sites of Victoria blue B than the Brilliant yellow.

(f) Photodegradation kinetics

In view of the analysis of degradation using Langmuir-Hineshel wood (L-H) kinetic model has been used by several authors for heterogeneous photocatalytic reaction [86]. The dye is adsorbed onto the spinel oxide surface until adsorption-desorption equilibrium is reached. After adsorption, the equilibrium centration of the dye solution is determined and it is taken as initial dye concentration for kinetic analysis. The influence of initial concentration of Victoria blue-B and Brilliant yellow on the photocatalytic degradation rate is described by pseudo-first order kinetics \[ \ln \frac{[C_0]}{C} = k't \], where \( k' \) is the pseudo-first order rate constant, \( C_0 \) is the initial concentration and \( C \) is the concentration of time \( t \) of these dyes. A plot of \( \ln \frac{C_0}{C} \) against time \( t \) for photodegradation is shown in Fig. 15(b) for Victoria blue-B and Brilliant yellow dye. A linear relation between the dye concentration and irradiation time has been observed. Rate constant was calculated from the graphs by \( k' = 2.303 \times \text{slope} \). The results of pseudo – first order rate constant \( k \) are depicted in Table VIII. It is observed that, higher is percent degradation, and higher is the rate constant. Also, it is noticed that the rate constant \( k \) of Victoria blue-B is higher than Brilliant yellow and its rate increases on doping of spinel oxide. This is due to Victoria blue-B is basic dye and strongly adsorbed on the surface of the spinel oxide. At basic pH the negative
surface of the spinel oxide with hydroxyl radical (OH) ions acts as an efficient trap for the photogenerated holes and hydroxyl are produced.

(g) Measurement of chemical oxygen demand (COD)

To determine the COD removal in spinel-sensitized photo oxidation, the Victoria blue-B and Brilliant yellow dye were tested. The measurements of the COD of the irradiated sunlight solution are generally used for monitoring the mineralization of these dyes. The result of COD has shown in Table VIII. From the results, it was found that COD decrease after photo-oxidation. This means that the dye decomposes to smaller organic intermediates that are still present in the solution, suggesting that prolonged illumination of sunlight (for 3h) can probably lead to complete mineralization.

(h) Mechanism of photo degradation

On the basis of experimental result, the photocatalytic degradation mechanism of Victoria blue-B and Brilliant yellow dyes by the undoped and dual doped spinel oxides under sunlight irradiation was proposed. On doping might have increased the rate of charge transport and flow of photo generated e⁻ and h⁺ in the spinel oxide under sunlight by taking example of say doped ZnFe₂O₄

\[
\begin{align*}
\text{Zn}_{0.953}\text{Cu}_{0.047}\text{Fe}_{1.940}\text{Mn}_{0.06}\text{O}_4 + \text{h}^+\text{Zn} &\rightarrow \text{Zn}_{0.953}\text{Cu}_{0.047}\text{Fe}_{1.940}\text{Mn}_{0.06}\text{O}_4 (\text{h}^+\text{VB} + \text{e}^-\text{CB}) \\
\text{Zn}_{0.953}\text{Cu}_{0.047}\text{Fe}_{1.940}\text{Mn}_{0.06}\text{O}_4 (\text{h}^+\text{VB}) + \text{H}_2\text{O} &\rightarrow \text{H}^+ + \text{OH}^- \\
\text{Zn}_{0.953}\text{Cu}_{0.047}\text{Fe}_{1.940}\text{Mn}_{0.06}\text{O}_4 (\text{h}^+\text{VB}) + \text{OH}^- &\rightarrow \text{OH}^- \\
\text{Zn}_{0.953}\text{Cu}_{0.047}\text{Fe}_{1.940}\text{Mn}_{0.06}\text{O}_4 (\text{e}^-\text{CB}) + \text{O}_2 &\rightarrow \\
\text{O}_2^- + \text{H}^+ &\rightarrow \text{HO}_2^- 
\end{align*}
\]
(e^\text{CB}) + \text{HO}_2^- + \text{H}^+ \rightarrow \text{OH}^- + \text{OH}^-

\text{Zn}_{0.953} \text{Cu}_{0.047} \text{Fe}_{1.940} \text{Mn}_{0.06} \text{O}_4 + \text{OH}^- + \text{HO}_2^- + \text{O}_2^- + h^+ \text{VB} \rightarrow \text{degradation product.}

(i) Reproducibility and recyclability of spinel oxides

As the stability of a photocatalyst is important to its applications, the recycle performance of undoped and dual doped spinel oxides has been explored. The reproducibility of the best catalyst for Victoria blue-B and Brilliant yellow in three-cycle experiment is performed. After each photodegradation experiment, the suspensions are centrifuged and wash with several times of distilled water to remove the adsorbed dye. The obtain catalyst was dried and heated upto 600°C for 2h and then cool to room temperature. The same catalyst was used for photodegradation of above dye. After three recycles, there was not a significant decrease for photocatalytic activity of undoped and dual doped spinel oxides.

4. Conclusion

(a) Nanocrystalline undoped and dual doped spinel oxides such as CoAl_2O_4,

\text{Co}_{0.953}\text{Zn}_{0.047}\text{Al}_{1.95}\text{Fe}_{0.05}\text{O}_4; \text{CoMoO}_4, \text{Co}_{0.957}\text{Fe}_{0.043}\text{Mo}_{0.954}\text{V}_{0.046}\text{O}_4; \text{ZnRh}_2\text{O}_4,

\text{Zn}_{0.949}\text{Bi}_{0.051}\text{Rh}_{0.951}\text{Dy}_{0.049}\text{O}_4; \text{ZnFe}_2\text{O}_4, \text{Zn}_{0.953}\text{Cu}_{0.047}\text{Fe}_{1.940}\text{Mn}_{0.06}\text{O}_4; \text{PrVO}_4,

\text{Pr}_{0.952}\text{Gd}_{0.048}\text{V}_{0.956}\text{Ru}_{0.044}\text{O}_4 were successfully synthesized using tartarate / oxalate or hydroxide precursors at 600°C. The tartarate/oxalate and hydroxide precursors are characterized by elemental analysis, X-ray fluorescence spectroscopy (XRF), infrared spectrum and thermal analysis.

(b) The X-ray diffraction of undoped and dual doped spinel oxides possess single spinel phased. CoAl_2O_4, ZnRh_2O_4, ZnFe_2O_4 and their doped spinels are cubic structure, while CoMoO_4 and PrVO_4 and their doped spinels are respectively
monoclinic and tetragonal structure. The Crystallite size for all spinel oxides are in the range of 15.86 to 62.50 nm.

(c) X-ray density is higher than apparent density for all spinels studied in the present work. This is attributed to the existence of pores, which depends on the sintering conditions. Scanning electron micrograph (SEM) showed an average grain size in the range of 29.96 to 68.07 nm.

(d) Temperature variation of d.c. electrical conductivity for undoped and dual doped spinel confirms semiconducting nature of sample. The activation energy (Ea) in the region B was higher than the region A. These studies showed that small polaron and electron hopping mechanisms take part in conductivity of samples investigated here i.e. Extrinsic mechanism, while at high temperature (afterTc) it show intrinsic conduction. However, activation energy Ea in the region B for dual doped spinel oxides are lower than in the region A. This is based on changes of the ionic distances in the spinel crystal structure.

(e) The thermoelectric power measurement for undoped and dual doped spinel oxides showed n-type semiconductor throughout the temperature range.

(f) The dielectric constant and dielectric loss (tan δ) decreases with increase in frequency in all undoped and dual doped spinel oxides. This is due space charge polarization and it decreases with increase in frequency and then reaches constant. The electron exchange $M^{2+} \rightarrow M^{3+}$ cannot follow alternating electric field variation. Dielectric loss (tan δ) at lower frequencies corresponds to high value of resistivity due to grain boundaries i.e. dielectric loss is directly proportional to the conductivity.
(g) The photocatalytic degradation on Victoria blue-B and Brilliant yellow under sunlight irradiation are found to be increase with dual doped spinel oxides. The presence of $M^{2+}$ ion at the octahedral site of spinel oxide will act as a recombination centre (i.e. photoinduced electron-hole pairs generation in presence of sunlight). The variable studied included the effect of pH, the amount of catalyst and dye concentration. Basic pH is found to be better than acidic pH. The degradation follows pseudo-first order kinetics. Since spinel oxides are stable in nature environments including water and photocatalysis environments, the spinel nanoparticles are long term stable and reusable.
5. References

33. JCPDS No. 82. 2252
34. JCPDS No. 21-0868
35. JCPDS No. 41-0134
36. JCPDS No. 74-2397
37. JCPDS no. 17-0879
53. G. Kianpour, M. S. Niasari and H. E. Madi, Microstru. 58 (2013) 120.
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**Table I:** Observed elemental and XRF data of precursor
Table II: Infrared spectral bands and their probable assignments for tartarate / Oxalate and hydroxide precursor

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<td>1229(m)</td>
<td>v_{as}C = O</td>
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<tr>
<td>1070 (m)</td>
<td>-</td>
<td>-</td>
<td>1051(m)</td>
<td>1093(m)</td>
<td>u_{C=O} (alcohol)</td>
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<tr>
<td>997 (w)</td>
<td>-</td>
<td>-</td>
<td>972(m)</td>
<td>1024(w)</td>
<td>u_{C=O} (alcohol) u(MoO₄₂)</td>
</tr>
<tr>
<td>-</td>
<td>920 (s)</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>891 (w)</td>
<td>-</td>
<td>-</td>
<td>904(w)</td>
<td>991(m)</td>
<td>v_{as}(C – O), δ(O – C – O) u(MoO₄₂)</td>
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<tr>
<td>-</td>
<td>866 (s)</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>-</td>
<td>-</td>
<td>827(m)</td>
<td>-</td>
<td>-</td>
<td>v_{M-OH} (deformed)</td>
</tr>
<tr>
<td>800 (m)</td>
<td>804(s)</td>
<td>-</td>
<td>871(m)</td>
<td>829(w)</td>
<td>v_{C-H wag}</td>
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<tr>
<td>732(s)</td>
<td>785(w)</td>
<td>-</td>
<td>746(m)</td>
<td>752(w)</td>
<td>v₂₅₃C – C</td>
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<tr>
<td>657(m)</td>
<td>675(w)</td>
<td>646(m)</td>
<td>621(m)</td>
<td>621(m)</td>
<td>v_{H - O - H}</td>
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<tr>
<td>553(w)</td>
<td>462 (w)</td>
<td>503(m)</td>
<td>551(m)</td>
<td>569(m)</td>
<td>v_{M – Ï€ , v_{C - C}}</td>
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s = small, m = medium, w = weak
### Table III: TGA and DTA data of dicarboxylate / hydroxide precursors under static air atmosphere

<table>
<thead>
<tr>
<th>Precursor</th>
<th>TGA</th>
<th>DTA</th>
<th>Predicted intermediates and final products</th>
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<td></td>
<td>% mass loss</td>
<td>Temp. range (°C)</td>
<td>peak temp. (°C)</td>
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<td></td>
<td>Obsd</td>
<td>calcd</td>
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<tr>
<td>(NH₄)₂[CoAl₂(C₄H₄O₆)(OH)₂].4H₂O</td>
<td>8.89</td>
<td>8.49</td>
<td>30-115</td>
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<td></td>
<td>9.62</td>
<td>9.28</td>
<td>115-245</td>
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<td></td>
<td>78.62</td>
<td>74.84</td>
<td>245-800</td>
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<td>(NH₄)Co(OH)(MoO₄)</td>
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<td>13.10</td>
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<td>18.72</td>
<td>17.69</td>
<td>125-750</td>
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<td>ZnFe₂(C₄H₄O₆)₄.4H₂O</td>
<td>8.66</td>
<td>8.55</td>
<td>30-180</td>
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<td></td>
<td>65.83</td>
<td>68.88</td>
<td>180-600</td>
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<tr>
<td>PrVO(C₂O₄)₂.5H₂O</td>
<td>4.15</td>
<td>4.03</td>
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<td></td>
<td>37.90</td>
<td>40.20</td>
<td>100-600</td>
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Table IV: Observed XRF and EDAX analysis of undoped and dual doped nanocrystalline spinels

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<th>Compounds</th>
<th>Metal analysis in wt % (±0.5)</th>
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<tr>
<td></td>
<td>Req</td>
<td>Found</td>
<td>Req</td>
<td>Found</td>
<td>Req</td>
<td>Found</td>
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<tr>
<td></td>
<td>Co</td>
<td>Zn</td>
<td>Al</td>
<td>Fe</td>
<td>Co</td>
<td>Zn</td>
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<tr>
<td>CoAl₂O₄</td>
<td>31.31</td>
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<td>-</td>
<td>30.50</td>
<td>29.30</td>
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<tr>
<td></td>
<td>31.29 (32.89)*</td>
<td>-</td>
<td>-</td>
<td>29.30 (29.99)</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Co₀.₉₅Zn₀.₀₄₇Al₁₀.₅₁Fe₀.₅₁O₄</td>
<td>31.45</td>
<td>1.72</td>
<td>1.70 (1.72)</td>
<td>29.45</td>
<td>29.33 (29.00)</td>
<td>1.56</td>
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<tr>
<td>CoMoO₄</td>
<td>26.92</td>
<td>-</td>
<td>-</td>
<td>43.83</td>
<td>43.12 (39.65)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>26.06 (26.67)</td>
<td>-</td>
<td>-</td>
<td>42.12 (40.10)</td>
<td>1.08</td>
<td>1.07 (1.09)</td>
</tr>
<tr>
<td>Co₀.₉₅Fe₀.₀₄₃Mo₀.₅₄V₀.₄₆O₄</td>
<td>26.30</td>
<td>1.10</td>
<td>1.09 (1.08)</td>
<td>42.24</td>
<td>42.12 (40.10)</td>
<td>1.08</td>
</tr>
<tr>
<td>ZnₐRh₂O₄</td>
<td>19.50</td>
<td>-</td>
<td>-</td>
<td>61.40</td>
<td>60.30 (59.56)</td>
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<tr>
<td></td>
<td>18.05 (18.50)</td>
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<td>-</td>
<td>58.12</td>
<td>58.10 (52.34)</td>
<td>2.30</td>
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<tr>
<td>Zn₀.₉₄₉Bi₀.₀₅₁Rh₁₀.₅₁Dy₀.₄₉O₄</td>
<td>17.96</td>
<td>3.08</td>
<td>3.06 (3.10)</td>
<td>58.12</td>
<td>58.10 (52.34)</td>
<td>2.30</td>
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<tr>
<td>ZnFe₂O₄</td>
<td>27.12</td>
<td>-</td>
<td>-</td>
<td>46.32</td>
<td>45.04 (42.21)</td>
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</tr>
<tr>
<td></td>
<td>25.74 (26.43)</td>
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<td>-</td>
<td>44.96</td>
<td>41.52 (41.94)</td>
<td>1.36</td>
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<tr>
<td>Zn₀.₉₅₃Cu₀.₀₄₇Fe₁₀.₉₄Mn₀.₄₆O₄</td>
<td>25.86</td>
<td>1.23</td>
<td>1.20 (1.21)</td>
<td>44.96</td>
<td>41.52 (41.94)</td>
<td>1.36</td>
</tr>
<tr>
<td>PrVO₄</td>
<td>55.07</td>
<td>2.91</td>
<td>2.90 (2.93)</td>
<td>18.81</td>
<td>17.71 (17.67)</td>
<td>1.71</td>
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<tr>
<td>Pr₀.₉₅₂Gd₀.₄₄₂V₀.₉₅₆Ru₀.₀₄₄O₄</td>
<td>51.81</td>
<td>-</td>
<td>-</td>
<td>19.91</td>
<td>18.19 (18.53)</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 dual doped nanocrystalline spinels

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<tr>
<th></th>
<th>CoAl₂O₄</th>
<th>Co₀.⁹₅Zn₀.₀⁴₇Al₁.₉₅Fe₀.₀₅O₄</th>
<th>CoMoO₄</th>
<th>Co₀.⁹₅Fe₀.₀₄₃Mo₀.₉₅V₀.₀₄₃O₄</th>
<th>ZnRh₂O₄</th>
<th>Zn₀.₉₄₉Bi₀.₀₅₁Rh₁.₉₅₁D₂₀.₀₄₉O₄</th>
<th>ZnFe₂O₄</th>
<th>Zn₀.₉₅₃Cu₀.₀₄₇Fe₁.₉₄₀Mn₀.₀₆O₄</th>
<th>PrVO₄</th>
<th>Pr₀.₉₅₂Gd₀.₀₄₈V₀.₉₅₆Ru₀.₀₄₄O₄</th>
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<td>Observed 'd' spacing values of nanocrystalline spinel (Å)</td>
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<tr>
<td>2.8697(42)*</td>
<td>2.8679(57)*</td>
<td>6.794 (8)*</td>
<td>6.794 (6)*</td>
<td>4.9294 (26)*</td>
<td>4.9513 (29)*</td>
<td>4.8597 (11)*</td>
<td>4.8545 (8)*</td>
<td>4.8650 (30)*</td>
<td>4.8075 (24)*</td>
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<tr>
<td>2.4416 (100)</td>
<td>2.4416 (100)</td>
<td>4.6768 (9)</td>
<td>4.6719 (9)</td>
<td>3.0174 (16)</td>
<td>3.0075 (16)</td>
<td>2.9800 (33)</td>
<td>2.9800 (23)</td>
<td>3.6837 (100)</td>
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<tr>
<td>2.0179 (18)</td>
<td>2.0274 (23)</td>
<td>3.8308 (19)</td>
<td>3.814 (27)</td>
<td>2.5687 (100)</td>
<td>2.5744 (100)</td>
<td>2.5391 (100)</td>
<td>2.5363 (100)</td>
<td>2.7477 (69)</td>
<td>2.7331 (55)</td>
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<td>1.8603 (15)</td>
<td>3.3960 (12)</td>
<td>3.3853 (13)</td>
<td>2.4597 (29)</td>
<td>2.4636 (16)</td>
<td>2.3073 (20)</td>
<td>2.1064 (16)</td>
<td>2.6049 (19)</td>
<td>2.5903 (18)</td>
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<td>1.6500 (16)</td>
<td>1.6549 (18)</td>
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<td>3.3582 (100)</td>
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<td>2.1397 (20)</td>
<td>1.7221 (18)</td>
<td>1.7203(16)</td>
<td>2.2951 (16)</td>
<td>2.2828 (19)</td>
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<td>1.5585 (40)</td>
<td>3.2853 (21)</td>
<td>3.2782 (32)</td>
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<td>1.6221 (35)</td>
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<td>1.5065 (32)</td>
<td>1.4908 (34)</td>
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<td>1.9498 (12)</td>
<td>1.9388 (12)</td>
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<td>1.3704 (12)</td>
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<td>1.4075 (12)</td>
<td>1.4071 (6)</td>
<td>1.8901 (55)</td>
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<td>1.3504 (15)</td>
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<td>1.3219 (10)</td>
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<td>2.6635 (19)</td>
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<td>1.2874 (8)</td>
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<td>1.6418(11)</td>
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<td>1.2368 (20)</td>
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<td>2.4416 (10)</td>
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<td>1.2737 (7)</td>
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<td>1.2185 (6)</td>
<td>1.227 (14)</td>
<td>1.2248 (6)</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 dual doped nanocrystalline spinels

<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 Dᵢ (g.cm⁻³)</th>
<th>Apparent density Dᵥ 1-D/Dᵢ (g.cm⁻³)</th>
<th>Porosity P= 1-D/Dᵢ %</th>
<th>Average particle size (from SEM) nm</th>
<th>Infrared spectral absorption band cm⁻¹</th>
<th>ν₁</th>
<th>ν₂</th>
<th>ν₃</th>
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<td>CoAl₂O₄</td>
<td>Cubic</td>
<td>0.807</td>
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<td>7.705</td>
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<td>0.864</td>
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<td>667 554 484</td>
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<td>Co₀.₉₅₉₅Zn₀.₀₄₇Al₁.₉₅Fe₀.₀₅O₄</td>
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<td>0.810</td>
<td>45.70</td>
<td>6.255</td>
<td>4.455</td>
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<td>0.834</td>
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<td>660 557 478</td>
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<tr>
<td>CoMoO₄</td>
<td>Monoclinic</td>
<td>a=1.026  b=0.928  c=0.708</td>
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<td>53.721</td>
<td>4.497</td>
<td>1.173</td>
<td>0.737</td>
<td>39.07</td>
<td>910 685 464</td>
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<td>a=1.025  b=0.926  c=0.706</td>
<td>62.50</td>
<td>52.342</td>
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<td>0.701</td>
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<td>952 661 437</td>
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<tr>
<td>ZnRh₂O₄</td>
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<td>6.059</td>
<td>7.219</td>
<td>1.300</td>
<td>0.819</td>
<td>35.96</td>
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<td>Zn₀.₉₄₉₅Bi₀.₀₅₁Rh₁.₉₅₁Dy₀.₀₄₉O₄</td>
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<td>0.712</td>
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<td>ZnFe₂O₄</td>
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<td>49.90</td>
<td>4.561</td>
<td>5.329</td>
<td>0.946</td>
<td>0.822</td>
<td>48.90</td>
<td>648 561 437</td>
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</tr>
<tr>
<td>PrVO₄</td>
<td>Tetragonal</td>
<td>a=0.₇₃₆  c=0.₆₄₆</td>
<td>41.83</td>
<td>5.471</td>
<td>4.844</td>
<td>1.512</td>
<td>0.687</td>
<td>44.44</td>
<td>1024 825 663</td>
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</tr>
<tr>
<td>Pr₀.₉₅₃₃Gd₀.₀₄₈V₀.₉₅₄Ru₀.₀₄₄O₄</td>
<td></td>
<td>a=0.₇₃₂  c=0.₆₄₃</td>
<td>60.65</td>
<td>2.521</td>
<td>4.978</td>
<td>2.16</td>
<td>0.566</td>
<td>64.44</td>
<td>1050 863 663</td>
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Table VII: Electrical conductivity data and dielectric properties of undoped and dual doped nanocrystalline spinels

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<th>Compounds</th>
<th>Conductivity measurements</th>
<th>Thermoelectric power measurements</th>
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<td>Temp. range (K)</td>
</tr>
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<td>CoAl_2O_4</td>
<td>A</td>
<td>322 - 641</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>641 - 862</td>
</tr>
<tr>
<td>Co_{0.95}Zn_{0.047}Al_{1.95}Fe_{0.05}O_4</td>
<td>A</td>
<td>312 - 625</td>
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<td></td>
<td>B</td>
<td>625 - 892</td>
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<tr>
<td>CoMoO_4</td>
<td>A</td>
<td>320 - 617</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>617 - 724</td>
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<tr>
<td>Co_{0.957}Fe_{0.043}Mo_{0.954}V_{0.046}O_4</td>
<td>A</td>
<td>304 - 531</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>531 - 714</td>
</tr>
<tr>
<td>ZnRh_2O_4</td>
<td>A</td>
<td>312 - 416</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>416 - 609</td>
</tr>
<tr>
<td>Zn_{0.949}Bi_{0.051}Rh_{1.951}Dy_{0.049}O_4</td>
<td>A</td>
<td>312 - 500</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>500 - 632</td>
</tr>
<tr>
<td>ZnFe_2O_4</td>
<td>A</td>
<td>297 - 588</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>588 - 980</td>
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<tr>
<td>Zn_{0.953}Cu_{0.047}Fe_{1.940}Mn_{0.06}O_4</td>
<td>A</td>
<td>308 - 568</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>568 - 877</td>
</tr>
<tr>
<td>PrVO_4</td>
<td>-</td>
<td>301 - 704</td>
</tr>
<tr>
<td>Pr_{0.952}Gd_{0.048}V_{0.956}Ru_{0.044}O_4</td>
<td>-</td>
<td>303 - 757</td>
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</table>
**Table VIII**: Photocatalytic details of undoped and dual doped nanocrystalline spinels

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Adsorption edge $\lambda$ (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>CoAl$_2$O$_4$</td>
<td>256</td>
<td>4.84</td>
<td>65.47</td>
<td>57.43</td>
<td>0.008</td>
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<tr>
<td>Co$<em>{0.953}$Zn$</em>{0.047}$Al$<em>{1.95}$Fe$</em>{0.05}$O$_4$</td>
<td>505</td>
<td>2.45</td>
<td>69.72</td>
<td>60.43</td>
<td>0.009</td>
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<td>CoMoO$_4$</td>
<td>571</td>
<td>2.17</td>
<td>53.68</td>
<td>51.05</td>
<td>0.006</td>
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<tr>
<td>Co$<em>{0.957}$Fe$</em>{0.043}$Mo$<em>{0.954}$V$</em>{0.046}$O$_4$</td>
<td>578</td>
<td>2.14</td>
<td>58.50</td>
<td>56.56</td>
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<td>ZnRh$_2$O$_4$</td>
<td>487</td>
<td>2.54</td>
<td>59.68</td>
<td>54.98</td>
<td>0.007</td>
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<td>Zn$<em>{0.949}$Bi$</em>{0.051}$Rh$<em>{1.951}$Dy$</em>{0.049}$O$_4$</td>
<td>496</td>
<td>2.50</td>
<td>65.62</td>
<td>57.92</td>
<td>0.009</td>
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<tr>
<td>ZnFe$_2$O$_4$</td>
<td>485</td>
<td>2.55</td>
<td>92.62</td>
<td>74.93</td>
<td>0.021</td>
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<td>Zn$<em>{0.953}$Cu$</em>{0.047}$Fe$<em>{1.946}$Mn$</em>{0.06}$O$_4$</td>
<td>508</td>
<td>2.44</td>
<td>95.31</td>
<td>82.20</td>
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<td>PrVO$_4$</td>
<td>378</td>
<td>3.28</td>
<td>41.89</td>
<td>35.56</td>
<td>0.004</td>
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<tr>
<td>Pr$<em>{0.952}$Gd$</em>{0.048}$V$<em>{0.956}$Ru$</em>{0.044}$O$_4$</td>
<td>385</td>
<td>3.22</td>
<td>44.85</td>
<td>41.85</td>
<td>0.004</td>
</tr>
</tbody>
</table>

VBB- Victoria blue-B, BY-Brilliant yellow
Mixed together Dilute sulphuric acid (to make just acidic)

Clear solution stirred vigorously
Maintained at 50°C

6% disodium tartarate solution

Mixed metal Tartarate precipitate

Distilled acetone (to get homogenous precipitate)

Stirred vigorously for 30 mins.

Filtered, washed with distilled water, acetone and dried

Mixed metal tartarate co precipitate (i.e. precursors)

Calcined at 600°C in static air atmosphere for 2 hrs. reground and recalcined at the same temperature

ZnFe$_2$O$_4$

(Similar method is used for dual doped spinel oxides)

Fig.1: Flowchart for the preparation of nanocrystalline Zinc ferrite by tartarate precursor method.
Fig. 2: Infrared spectra for precursor
(a) \((\text{NH}_4)_2[\text{CoAl}_2(\text{C}_4\text{H}_6\text{O}_6)_4(\text{OH})_2].4\text{H}_2\text{O}\), (b) \((\text{NH}_4)\text{Co(OH)(MoO}_4\),
(c) \(\text{ZnRh}_2(\text{OH})_8.2\text{H}_2\text{O}\), (d) \(\text{ZnFe}_2(\text{C}_4\text{H}_4\text{O}_6)_4.4\text{H}_2\text{O}\), (e) \(\text{PrVO}(\text{C}_2\text{O}_4)_2.5\cdot\text{H}_2\text{O}\)
Fig. 3: TGA and DTA curves for dicarboxylate precursor in normal air atmosphere.
(a) \((\text{NH}_4)_2\text{[CoAl}_2\text{(C}_4\text{H}_4\text{O}_8)_4\text{(OH)}_2]\text{4H}_2\text{O}\), (b) \((\text{NH}_4)\text{Co(OH)(MoO}_4]\),
(c) \text{ZnRh}_2\text{(OH)}_8\text{2H}_2\text{O}\), (d) \text{ZnFe}_2\text{(C}_4\text{H}_4\text{O}_6)_4\text{4H}_2\text{O}\), (e) \text{PrVO(C}_2\text{O}_4)_2\text{5H}_2\text{O}\)
Fig. 4: Energy dispersive X-ray spectrum (EDAX) of undoped and dual doped nanocrystalline spinels
(a) CoAl$_2$O$_4$, (b) Co$_{0.953}$Zn$_{0.047}$Al$_{1.95}$Fe$_{0.05}$O$_4$, (c) CoMoO$_4$, (d) Co$_{0.957}$Fe$_{0.043}$Mo$_{0.954}$V$_{0.046}$O$_4$, (e) ZnRh$_2$O$_4$, (f) Zn$_{0.949}$Bi$_{0.051}$Rh$_{1.951}$Dy$_{0.049}$O$_4$
Fig. 5: Energy dispersive X-ray spectrum (EDAX) of undoped and dual doped nanocrystalline spinels
(a) ZnFe$_2$O$_4$, (b) Zn$_{0.953}$Cu$_{0.047}$Fe$_{1.940}$Mn$_{0.06}$O$_4$,
(c) PrVO$_4$, (d) Pr$_{0.952}$Gd$_{0.048}$V$_{0.956}$Ru$_{0.044}$O$_4$. 
Fig. 6: X-ray diffraction patterns of undoped and dual doped nanocrystalline spinels
Fig. 7: Scanning electron micrographs (SEM) of undoped and dual doped nanocrystalline spinels.
  
  (a) CoAl$_2$O$_4$, (b) Co$_{0.953}$Zn$_{0.047}$Al$_{1.95}$Fe$_{0.05}$O$_4$, (c) CoMoO$_4$, 
  (d) Co$_{0.957}$Fe$_{0.043}$Mo$_{0.954}$V$_{0.046}$O$_4$, (e) ZnRh$_2$O$_4$, (f) Zn$_{0.949}$Bi$_{0.051}$Rh$_{1.951}$Dy$_{0.049}$O$_4$
Fig. 8: Scanning electron micrographs (SEM) of undoped and dual doped nanocrystalline spinels. (a) ZnFe$_2$O$_4$, (b) Zn$_{0.953}$Cu$_{0.047}$Fe$_{1.940}$Mn$_{0.06}$O$_4$, (c) PrVO$_4$, (d) Pr$_{0.952}$Gd$_{0.048}$V$_{0.956}$Ru$_{0.044}$O$_4$. 
Fig. 9: Plot of log $\sigma$ against $T^{-1}$ of undoped and doped spinel oxides
Fig. 10: Plot of thermoelectric power, $\mu$ (volts K$^{-1}$) against temperature, T(K) for (a) undoped (b) doped spinel oxides.
Fig. 11: Plot of variation of dielectric constant ($\varepsilon'$) with frequency for (a) undoped and (b) doped oxides.

(a) UNDOPED SPINEL OXIDES

(b) DUAL DOPED SPINEL OXIDES
Fig. 12: Plot of variation of dielectric loss (tan δ) with frequency for (a) undoped and (b) doped oxides.
Fig. 13: UV-DRS Plot for (a) undoped and (b) dual doped spinel 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 dual doped nanocrystalline spinels.