Chapter V
CHAPTER V

Influence of A- and B-site cations on the physicochemical properties of perovskite-type nanooxides

1. Introduction

Nanomaterials like perovskite type oxides with the formula ABO$_3$ are highly interesting materials because of their technological importance and potential applications [1-3]. The partial substitution of ions at A and B site is possible, leading to a variation of properties, while preserving the perovskite structure. Furthermore, deficiencies in sites A and B in the oxygen anions are common, resulting in materials with defect. Generally, the oxygen vacancies are directly related to different properties observed in perovskites, as electrical, magnetic, catalytic activity and photoluminescence [4-10].

A perovskite-type oxide has an ABO$_3$ crystal structure, where large ionic radius cations are 12 coordinate to oxygen atoms and occupy A-sites, and smaller ionic radius cations are 6 coordinate to oxygen atoms and occupy B-sites [11]. For an un-substituted perovskite catalytic activity is predominantly attributed to the metal ion at the B-site. The A-site metal has a strong effect on stability, providing a possibility for improving catalytic activity through synergetic interactions with metals at the B-sites [11]. The partial substitution of the A and B ions is possible, which leads to a change in the properties while preserving the perovskite structure.

The catalytic activity of perovskite materials is mainly determined by the transition metal at B-site. Therefore, valence and vacancy of the transition metal ions at B-site is important to enhance the catalytic activity. A combination of two different ions at the B-site brings about synergistic effects and can also improve the performance of different physical properties. The mixed-valent perovskite oxide have
attracted considerable attention in recent years because of the observation of electronic, magnetic and catalytic related phenomena. Effects of A and B substitution on the Curie temperature ($T_c$) and other physical properties of $\text{La}_{1-x} (\text{Ca, Sr})_x\text{Mn}_{1-y}\text{Co}_y \text{O}_3$ have been reported by some workers [10, 12-18]. In compounds $\text{La}_{1-x} \text{A}_x \text{Mn}_{1-y}\text{Co}_y$ there are different states of oxidation of Mn and Co that depend on the method of material preparation.

In recent years, stannates, manganates, aluminates and titanates are important perovskite materials, which have been extensively investigated due to their interesting properties such as Ferroelectricity, high transition-temperature superconductivity, piezoelectricity, photoelectrochemical sensitivity, and photocatalytic activity [4, 19-31]. For instance, doping of these perovskites with transition metals and rare earths has provided the formation of materials with interesting structural, magnetic and semiconducting properties [19, 27, 29, 31, 32]. These materials have been found to be interesting for a number of potential applications industry such as components of dielectric ceramics; multifunctional signal sensors to detect temperature, humidity, and gas; as negative electroactive materials for long life energy storage applications, and in the fabrication of ceramic boundary-layer capacitors etc. [33].

Over the past few decades, photocatalysis has attracted considerable attention because it can potentially resolve the problem of environmental contamination and energy exhaustion by facilitating the decomposition of pollutants and water splitting[34-36]. Generally, photocatalysts are required to high optical absorption properties, high surface areas, high crystallinity, high chemical stability etc. A lot of studies have been carried out with the aim of enhancing the photocatalytic activity of photocatalyst by adjusting their size and shape using various synthesis methods [4, 37-39].
In the present work, the simultaneous substitution of rare earth at the A-site and transition metal at the B-site in a stannate, manganate, aluminate and titanate lattice will be examined to determine their effect on structural, electrical and photocatalytic activity. A series of $A_{1-x}Ln_xB_{1-y}M_yO_3$ (M = transition metals) perovskite were prepared and characterized by X-ray diffraction, scanning electron microscopy, far infrared spectra, d.c. electrical conductivity, dielectric constant measurements. The photocatalytic activity of Victoria blue-B and Brilliant yellow dyes was evaluated by spectrophotometrically. The effect of time, amount of catalyst, concentration of dyes and pH value on the photocatalytic performance of above perovskite oxides in the photodegradation of Victoria blue-B and Brilliant yellow under sun light irradiation was deeply investigated, too.

2. Experimental

2.1 Synthesis of Precursors:

The required amount of metal salts was dissolved in distilled water and then added disodium tartarate or ammonium hydroxide solution at appropriate pH. Quantities of reactants were calculated according to the stoichiometry in the final product.

2.1.1 Strontium-tin hydroxide, $\text{SrSn(OH)}_6\cdot0.5\text{H}_2\text{O}$

4.435 g $\text{SnCl}_2\cdot2\text{H}_2\text{O}$ was dissolved in 5 mL concentrated hydrochloric acid (HCl) and boil it, to form clear solution. Dilute the solution to ~ 25 mL with distilled water.

In another beaker 5.2416 g of strontium chloride ($\text{SrCl}_2\cdot6\text{H}_2\text{O}$) was dissolved in 10 mL distilled water. Then these two solutions were mixed thoroughly on a magnetic stirrer and to this ammonium hydroxide solution (0.1M $\text{NH}_4\text{OH}$) was added drop by drop until the precipitation is complete. The pH of the medium was maintained at ≤ 9. The grey precipitate (i.e. $[\text{SrSn(OH)}_6\cdot0.5\text{H}_2\text{O}]$) was then digested at 90°C for one hour. The solution was filtered and washed with 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°C for 24 h and then ground with the help of agate mortar. The obtained powder samples were restore in a desiccator. Yield = 7.727 g.

Similar procedure was used for the synthesis of 10 wt% doped Strontium-tin hydroxide precursor by taking stoichiometric amount of europium chloride (0.507 g) and cobalt chloride (0.467 g) as dopant.

The flow sheet diagram for precursor and subsequent conversion to substituted perovskite nanooxides is depicted in Fig. 1.

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

2.1.2. Samarium - manganese tartarate two hydrates

\(\text{SmMn}(\text{C}_4\text{H}_4\text{O}_6)_{2.5}.2\text{H}_2\text{O}\)

This precursor was prepared by taking \(\text{Sm(NO}_3\text{)}_3.6\text{H}_2\text{O}\) (10.5282 g), and \(\text{MnCl}_2.4\text{H}_2\text{O}\) (4.688 g) in double distilled water (50 mL). To this disodium tartarate solution (13.625 g in 50 mL distilled water) was added slowly with stirring, till a permanent precipitate was occurred. The white coloured precipitate was obtained. The precipitate was filtered and washed with distilled water and then with acetone to speed up the drying. It was air dried at ambient temperature.

Yield: 14.834 g.

Using same procedure, the synthesis of 10 wt% doped samarium-manganese tartarate precursor was done by taking stoichiometric amount of bismuth nitrate (0.944 g) and copper nitrate (0.470 g) as dopant.
2.1.3 Neodymium aluminium tartarate two hydrate,

\[(\text{NH}_4)_2[\text{NdAl(C}_4\text{H}_4\text{O}_6)\text{O}_4\text{(OH)}_2]\cdot 2\text{H}_2\text{O}\]

This precursor was prepared by the coprecipitation method. Neodymium nitrate (10.00 g) and aluminium nitrate (10.00 g) were dissolved in minimum amount of water and mixed with an aqueous solution of tartaric acid (40.00 g), in the proportion of 1:1:4 [Nd(III) : Al(III) : Tartaric acid] ratio. Ethanol was added to the final solution until a pink precipitate was formed. The pH was raised to 6 by adding NH\(_4\)OH: Ethanol (1:1). After 24 hr at 4\(^\circ\)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 = 24.582 g.

Similar procedure was used for the synthesis of 10 wt% doped neodymium aluminium tartarate precursor by taking stoichiometric amount of dysprosium nitrate (0.542 g) and ferric nitrate (0.485 g) as dopant.

2.1.4. Zinc - titanium - tartarate one and half hydrate.

\[\text{ZnTi(C}_4\text{H}_4\text{O}_6)\text{O}_2\cdot 1.5\text{H}_2\text{O}\]

This precursor was prepared by the coprecipitation method by taking Zn(NO\(_3\))\(_2\)\cdot 6\text{H}_2\text{O} (9.223 g), and TiCl\(_3\).x\text{H}_2\text{O} (4.786 g) in double distilled water (50 mL). To this disodium tartarate solution (17.881 g dissolved in 25 mL distilled water) was added slowly with stirring, till a permanent light yellow coloured precipitate was occurred. The precipitate was filtered and washed with distilled water and air dried at ambient temperature. Yield = 26.394 g.

Similar procedure was used for the synthesis of 10 wt% doped zinc titanium tartarate precursor by taking stoichiometric amount of zirconyl nitrate (0.550 g) and terbium chloride (0.885 g) as dopant.
2.2 Synthesis of nanosized substituted perovskite compounds

The above precursors were decomposed and calcined slowly at 800°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 achievement a complete decomposition of precursors. 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 unsubstituted perovskites such as SrSnO$_3$; SmMnO$_3$; NdAlO$_3$, and ZnTiO$_3$ and their respective substituted nanooxides such as Sr$_{0.953}$Eu$_{0.047}$Sn$_{0.953}$Co$_{0.047}$O$_3$; Sm$_{0.948}$Bi$_{0.052}$Mn$_{0.965}$Cu$_{0.035}$O$_3$; Nd$_{0.954}$Dy$_{0.046}$Al$_{0.954}$Fe$_{0.046}$O$_3$; and Zn$_{0.957}$Tb$_{0.043}$Ti$_{0.960}$Zr$_{0.040}$O$_3$; were restored in a desiccator.

2.3 Physical analysis

The experimental details for characterization of precursors and perovskite oxides by elemental analysis, infrared spectra, thermal analysis, X-ray powder diffraction (XRD) density measurement, scanning electron microscopy (SEM), Energy dispersive X-ray analysis (EDAX), X-ray fluorescence spectroscopy (XRF), direct current electrical conductivity, thermoelectric power measurements, dielectric properties, UV-visible diffuse reflectance spectroscopy are explained in chapter II.

2.4 Photocatalytic activity

The photocatalytic activities of unsubstituted and substituted perovskite catalysts were evaluated by the degradation of two types of water-soluble dyes which include Victoria blue-B and Brilliant yellow under sunlight irradiation. The detail experiment was explained in chapter II. The reaction was done in a homemade reactor.
Running water was passed through the double wall to cool the reaction solution. The suspensions for the photochemical reactor by adding various perovskite nanopowders to a known concentration of dye solution. All experimental conditions were kept constant as follows:

50 ml of the suspension, 20 mg or 100 mg / L of initial dye concentration, 50 mg of photo catalyst and vigorously stirred with magnetic stirrer under sun light irradiation. The photocatalytic reaction lasted 2 h. Samples (~10 ml) for analysis were withdrawn through pipettes every 20 min., and immediately centrifuged. Absorption of the supernatant solution and initial solution (kept in dark) was determined, respectively using a UV-vis spectrophotometer at the maximum absorption wavelength of these two dyes. Percent degradation rate (De) was calculated as De = (Co - C) / Co x 100, where Co shows initial absorbance and C shows absorbance at time t. At least two catalytic experiments were carried out for each condition, averaging the results.

3. Results and Discussion

3.1 Characterization of tartarate or hydroxide precursors

Incoprecipitation process, it is necessary to optimize the following conditions; (a) the mole ratio of the different salts; (b) the pH of the solution, (c) the experimental conditions such as solution temperature, the precipitation age time, the stirring etc.

A quantitative tartarate or hydroxide precursors are from the saturated metal chloride or nitrate solution rare earth, transition metal, tin and alkaline-earth salts with slow addition of 3% sodium tartarate or ammonium hydroxide in stoichiometric proportions. The C, H analysis was carried out microanalytical techniques and metal analysis by X-ray fluorescence spectroscopy (XRF) of these precursors. The observed elemental analysis of Strontium-stannate hydroxide, SrSn(OH)₆.0.5H₂O; Samarium – manganese tartarate dihydrate SmMn(C₄H₄O₆)₂.5.2H₂O; Neodymium-aluminium tartarate dihydrate (NH₄)₂[NdAl(C₄H₄O₆)]₄(OH)₄. 2H₂O; Zinc-titanium tartarate one
and half hydrate ZnTi(C₄H₄O₆)₂.₅ .1.5H₂O were presented in Table I. It is good agreement with the calculated values. The thermal analysis measurements confirm the presence of the water of hydration of these precursors.

The infrared spectrum (Fig. 2) and their probable band assignments of fundamental frequencies for tartarate group, hydroxyl group, and metal-oxygen bonds are depicted in Table II. The infrared spectrum of these precursors showed a broad band at 3380cm⁻¹ corresponding to the weakly bonded water of crystallization and intense bands at 1562 cm⁻¹ due to νasy (C=O) and band at 1367 cm⁻¹ due to νsy (C-O). These values indicate the presence of coordinated carboxylate group [40]. While other bands, which are all combination band may be assigned to the difference normal modes of vibrations of the carboxylate group [40, 41]. A chain like polymeric octahedral structures has been assigned to these precursors[42].

The infrared spectrum of SrSn(OH)₆.0.5H₂O(Fig.2a) show characteristic vibrations in the region 400-4000 cm⁻¹. The presence of -OH group present in the sample was confirmed by the three mode of vibration at 3338, 1622 and 856 cm⁻¹, which are assigned as the stretching, bending and in-plane deformation of water molecule [43-45].

The TGA and DTA curve for SrSn(OH)₆.0.5H₂O, SmMn(C₄H₄O₆)₂.₅.2H₂O, (NH₄)₂[NdAl(C₄H₄O₆)]₃(OH)₂].2H₂O and ZnTi(C₄H₄O₆)₂.₅.1.5H₂O under static air atmosphere is shown in Fig. 3. The dehydration of these precursors can be detected on DTA curve at around 90⁰C. The TGA curve showed weight loss for dehydration step up to 150⁰C corresponding to loss of water molecules. The observed mass loss and corresponding temperature ranges are depicted in Table III. The oxidative decomposition of these precursors was indicated by the presence of strong peak on DTA curve at around 330⁰C. The TGA curve showed a single step of weight loss within temperature range 150-800⁰C except Nd-Al tartarate precursor, which show two step
weight loss; first at 150\(^0\)C-240\(^0\)C and second at 240-750\(^0\)C. The observed mass loses are reasonable agreement with the calculated values (Table III)

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 Strontium – stannate hydroxide

\[
\text{SrSn(OH)}_60.5\text{H}_2\text{O} \xrightarrow{50-140^0\text{C}} \text{SrSn(OH)}_6 + 0.5\text{H}_2\text{O}
\]
\[
\text{SrSn (OH)}_6 \xrightarrow{140-800^0\text{C}} \text{SrSnO}_3 + 3\text{H}_2\text{O}
\]

b) Samarium – Manganese tartarate

\[
\text{SmMn(C}_4\text{H}_4\text{O}_6)_{2.5}2\text{H}_2\text{O} \xrightarrow{30-150^0\text{C}} \text{SmMn(C}_4\text{H}_4\text{O}_6)_{2.5} + 2\text{H}_2\text{O}
\]
\[
\text{SmMn(C}_4\text{H}_4\text{O}_6)_{2.5} \xrightarrow{150-800^0\text{C}} \text{SmMnO}_3 + 4\text{CO}_2\uparrow + 3\text{CH}_4\uparrow + 3\text{CO}\uparrow
\]

c) Neodymium – aluminium tartarate

\[
(\text{NH}_4)_2[\text{NdAl(C}_4\text{H}_4\text{O}_6)_{4}(\text{OH})_2].2\text{H}_2\text{O} \xrightarrow{30-100^0\text{C}} (\text{NH}_4)_2[\text{NdAl(C}_4\text{H}_4\text{O}_6)_{4}(\text{OH})_2] + 2\text{H}_2\text{O}\uparrow
\]
\[
(\text{NH}_4)_2[\text{NdAl(C}_4\text{H}_4\text{O}_6)_{4}(\text{OH})_2] \xrightarrow{100-240^0\text{C}} [\text{NdAl(C}_4\text{H}_4\text{O}_6)_{4}] + 2\text{H}_2\text{O} + 2\text{NH}_3\uparrow
\]
\[
[\text{NdAl(C}_4\text{H}_4\text{O}_6)_{4}] \xrightarrow{240-750^0\text{C}} \text{NdAlO}_3 + \text{CO}_2\uparrow + \text{CH}_4\uparrow + \text{CO}\uparrow
\]

d) Zinc – titanium tartarate

\[
\text{ZnTi(C}_4\text{H}_4\text{O}_6)_{2.5}1.5\text{H}_2\text{O} \xrightarrow{30-150^0\text{C}} \text{ZnTi(C}_4\text{H}_4\text{O}_6)_{2.5} + 1.5\text{H}_2\text{O}\uparrow
\]
\[
\text{ZnTi(C}_4\text{H}_4\text{O}_6)_{2.5} \xrightarrow{150-800^0\text{C}} \text{ZnTiO}_3 + \text{CH}_4\uparrow + \text{C}_2\text{H}_5\uparrow + \text{CO}_2\uparrow
\]

3.2 Characterization of A- and B-site substituted perovskite type oxides

3.2.1 Compositional analysis:

The tartarate or hydroxide precursor are calcined in oxygen atmosphere at 800\(^0\)C for two hours to produce respective perovskite oxides. These oxides are then reground and recalcined at same temperature for another two hours. The obtained unsubstituted and substituted perovskite oxides such as \(\text{SrSnO}_3,\) \(\text{Sr}_{0.953}\text{Eu}_{0.047}\text{Sn}_{0.953}\text{Co}_{0.047}\text{O}_3;\) \(\text{SmMnO}_3,\) \(\text{Sm}_{0.948}\text{Bi}_{0.052}\text{Mn}_{0.965}\text{Cu}_{0.035}\text{O}_3;\) \(\text{NdAlO}_3,\) \(\text{Nd}_{0.954}\text{Dy}_{0.046}\text{Al}_{0.954}\text{Fe}_{0.046}\text{O}_3;\) \(\text{ZnTiO}_3,\) \(\text{Zn}_{0.957}\text{Tb}_{0.043}\text{Ti}_{0.960}\text{Zr}_{0.040}\text{O}_3\) are characterized at
the first stage by the metal analysis. The X-ray fluorescence spectroscopy (XRF) and
the energy dispersive X-ray analysis (EDAX) are used to confirm the presence of metal
species in the same cationic ratio as initially used and the observed compositions
are summarized in Table IV. They are found to be \( \pm 0.5\% \) of nominated value. This
suggests the stoichiometry in the compounds is perfectly maintain within the
experimental errors \(<1\%\).

The EDAX spectrum of unsubstituted and substituted perovskite oxides are
shown in Fig. 4 and 5. Peaks in these spectrum show all cations present in each
perovskite. No other peaks are evident.

3.2.2 X-ray studies

The X-ray diffraction pattern (XRD) of unsubstituted and substituted perovskite
oxides are shown in Fig. 6. The XRD pattern do not show any secondary phase. \( \text{SrSnO}_3, \)
\( \text{Sr}_{0.953}\text{Eu}_{0.047}\text{Sn}_{0.953}\text{Co}_{0.047}\text{O}_3; \) and \( \text{NdAlO}_3, \text{Nd}_{0.954}\text{Dy}_{0.046}\text{Al}_{0.954}\text{Fe}_{0.046}\text{O}_3 \) are found
to cubic structure, while \( \text{SmMnO}_3, \) and \( \text{Sm}_{0.948}\text{Bi}_{0.052}\text{Mn}_{0.965}\text{Cu}_{0.035}\text{O}_3 \) is orthorhombic.
The XRD pattern of \( \text{ZnTiO}_3 \) and \( \text{Zn}_{0.957}\text{Tb}_{0.043}\text{Ti}_{0.960}\text{Zr}_{0.040}\text{O}_3 \) can be indexed by a
hexagonal structure. The experimentally observed d-spacing values and relative
intensities (Table V) are compared with those reported in literature [46-49]. From d
value we calculate the lattice parameter and unit cell volume. The unit cell volume per
formula unit, as the number of formula units per unit cell is different for the four
structure described (i.e. Cubic, rhombohedral, orthorhombic and hexagonal structure).

The lattice parameter, unit cell volume, average cation sizes at A-site of
perovskite and mismatch factor \( \sigma^2 \) for each compound are listed in Table VI. It is seen
that the observed lattice parameter and unit cell volume for all samples are not change
except \( \text{SmMnO}_3 \) and its substituted compound as compared to the reported ones [46-
49] (see Table VI). The Cu substituting in \( \text{SmMnO}_3 \) will change \( \text{Mn}^{3+} - \text{Mn}^{4+} \) ratio and
interaction of Mn-Mn. The most stable state of Cu is \( \text{Cu}^{2+} \) and the radius of \( \text{Cu}^{2+} \) (6-
Coordinated) is about 0.73Å. This is much larger than the radius of Mn$^{3+}$ (0.645Å) and Mn$^{4+}$ (0.53Å) [52]. B-site substituting with Cu$^{2+}$ in SmMnO$_3$ will lead to an expansion of the unit cell volume rather than a contraction.

In perovskite (ABO$_3$) the size of cation on the A-site influences a large effect on the crystal symmetry significantly and has 12 coordinated cation, while that of smaller cation on the B-site does not change the symmetry and has six coordinated cation but change the lattice volume proportionally. Most material characterized as perovskite are not cubic due to distortions or tilt of the oxygen octahedra surrounding the B-site ions. The B-ion might also be too small to fill out the octahedral space.

Rodrigues and Ati field [50] argued that size differences between various A-site ions induced local distortions and stresses in structure. The quantitative description of this effect was given in terms of the variance of the cation radii distribution, \( \sigma^2 = \sum \{x|R_A|^2 - <R_A>^2\} \). Here, \( x \) is the fractional occupancies for the different cation at A-site species of the perovskite; \( R_A \) is their ionic radii, while \( <R_A> \) is the average size of the cations. The effect of mismatch factor (\( \sigma^2 \)) for different cation of substituted perovskite compounds have been calculated and are listed in Table VI. The standard ionic radii [51, 52] for different cation such as Sr$^{2+}$ (1.310Å$^0$), Eu$^{3+}$ (1.120Å$^0$), Sm$^{3+}$ (1.132Å$^0$), Bi$^{3+}$ (1.170Å$^0$), Nd$^{3+}$ (1.163Å$^0$), Dy$^{3+}$ (1.033Å$^0$), Zn$^{2+}$ (0.90Å$^0$) and Tb$^{3+}$ (1.095Å$^0$) are used to calculate average cation sizes \( <R_A> \) and mismatch factor (\( \sigma^2 \)) for eight coordination in case of the orthorhombic or cubic perovskite. As we can carefully seen from Table VI, the average cation size of cations at A-site of perovskite \( <R_A> \) is less than 1.21Å$^0$, which suggests the absence of cooperative long range Jahn-Teller distortion in the compounds [53]. However, the possibility of short length dynamical Jahn-Teller distortion cannot be excluded [54].

The additional disorder is created by substitution of small amount of cations at A-site perovskite, and they may be arising from the size mismatch factor (\( \sigma^2 \)) between
the A-site cation [50]. We have observed that the mismatch factor \((\sigma^2)\) varies with the compounds (See Table VI). This is due to segregation of the A-site cations, as a result of the large disparities in size, so that the compounds are no longer microscopically homogeneous, although they appear to be single phases by powder X-ray diffraction. It is therefore concluded that, the given constant A-site cation average radius \(<R_A> = 1.21\text{Å}\), the variation of the A-site disorder as characterized by variance mismatch factor \((\sigma^2)\) causes no change in the crystal structure. In addition to these effects, the strain field associated with the local displacement of oxygen ion presumable becomes so small that the system does not undergo a chemical phase separation. The local oxygen displacement, \(Q\) was calculated by using the relation [55]\(Q = \sqrt{2} \left(<R_A^2> - <R_A>^2\right)\). The \(Q\) values are observed in the range 0.0001006 to 0.0022867. It concludes that, there is a negligible amount of oxygen displacement occurs in all compounds.

Perovskite type structure with cubic symmetry is regarded as an ideal perovskite structure with the highest phase stability[56]. In order to measure the deviation of the present compounds from the ideal cubic symmetry, Goldschmidt tolerance factor \((t)\) [57]were calculated by using the relation \(t = \left[<R_A> + R(o)\right] / \sqrt{2} \left[<R_B> + R(o)\right]\) where \(t = \text{tolerance factors}, R(o) = 1.40\text{Å} \) is the ionic size of the oxide ion \(O^{2-}\) (for six coordinated radii), \(<A>\) and \(<B>\)are mean ionic sizes of ions at A-and B-site respectively, for the perovskite structure [51,52]. Tolerance factors \((t)\) are listed in Table VI.

When tolerance factor \((t)\) is in the range of 0.95 and 1.04 defined by the theoretical calculations, corresponds to the stable undistorted cubic structure [57, 58]. As we noticed from Table VI, the tolerance factor \((t)\) values for unsubstituted and substituted perovskite oxide are in the range from 0.760 to 0.937, which is lower than 0.95. However, due to transformation of some \(M^{3+}\) to \(M^{4+}\) caused by partial substitution at B-site of perovskite oxides, in the lattice via. electronic charge compensation.
under consideration of the existence of smaller size of cations at the B-site of perovskite, tolerance factor (t) still significantly below 0.95. These decreased tolerance factors can enhance a distortion of this perovskite structure. In summary, as A-site doped by smaller cation ions, the structure changes from the almost perfect cubic to the less symmetric orthorhombic or hexagonal structure.

Similarly, distorted perovskite structure can be calculated be in other way as follows; For the case of the largest A-site cation of perovskite type oxide, the value of lattice constant a is almost equal to that of b and c / √2, indicating an approximate cubic structure. But, with a smaller ion substitution at the A-site cation the structure deviated from cubic and was closer to orthorhombic or hexagonal. Quantitative evaluation of the deviation from ideal symmetric structure by D, defined as [59]:

\[
D = \frac{1}{3} \sum_{i=1}^{3} \left( \frac{|a_i - \bar{a}|}{\bar{a}} \right) \times 100
\]

Where, \(a_1 = a\), \(a_2 = b\), \(a_3 = \frac{c}{\sqrt{2}}\) and \(\bar{a} = (abc \sqrt{2})^{1/3}\)

The D values of substituted perovskite are in the range 0.839 to 1.279. If the D value is near to zero, then cubic structure observed and if D is larger value, then distorted structure observed. Therefore on the basis of this all unsubstituted and substituted perovskite oxides are always cubic distorted structure.

The lattice distortion observed is caused by the partial replacement of B-site cation of perovskite by other cation. Departure from average radius \(<R>\) of B ions at the dopant site would subject the neighboring B–O bonds to a centric push or pull. For a low concentration of dopant (substituent), the decrease of the average B-O-B bond angle and increase of B-O bond length is observed. Only when the ion radius at the dopant is smaller than the B-site cation radius, will the neighboring B-O bonds stretch, resulting in an increase of average B-O-B bond angle. The average radius of B-site cation ion \(<R_B>\) is calculated for unsubstituted perovskite type stannate = 0.810Å⁰, manganate =
0.580Å aluminate = 0.535Å and titanate = 0.740Å. The average radius of B-site substituted ions \(R_B\) is also calculated for stannate = 0.804Å, manganate = 0.585Å, aluminate = 0.546Å, and titanate = 0.744Å. Therefore, with these smaller ionic size cation doping (substituting) in respective stannate, manganate, aluminate and titanate at the B-site, then stretch the neighboring B-O-B bonds, thereby, the tolerance factor \(t\) decreases correspondingly, (See Table VI). Thus, with B-site doping, the crystal structure transition from cubic to distorted cubic (Orthorhombic or hexagonal) occurs in these compounds.

### 3.2.3 Particulate Properties:

The crystallite size of these perovskite calculated using the Scherrer method through the XRD profiles and is listed in Table VII. The crystallite size for unsubstituted and substituted perovskite are in the range between 36.8 nm to 60.25 nm. From crystallite sizes we also calculated the surface area and are depicted in Table VII. The surface area found in the range of 1.02 to 81.86 m\(^2\)/g.

Using the values of lattice parameter, we also calculate the particulate properties like X-ray density \((D_x)\), apparent density \((D)\) and porosity \((P)\) for all perovskite compounds are summarized in Table VII. It can be noticed that the observed apparent density is lower than the X-ray density. This may be due to the existence of pores, which were formed and developed during sample synthesis.

The morphology of the particles formed was examined by scanning electron micrographs (SEM) for all unsubstituted and substituted perovskite samples (Fig. 7 and 8). It can be observed that the particles have a spherical morphology. The particles connect with other to form a large network system with irregular sizes and shape (Fig. 7 (a) and (b)). The grain shape of SmMnO\(_3\) and Sm\(_{0.948}\)Bi\(_{0.052}\)Mn\(_{0.965}\)Cu\(_{0.035}\)O\(_3\) (Fig. 7(c) and (d)) has spherical, but less degree of agglomeration. It contraststo this, the small spherical grains are observed for unsubstituted and substituted aluminate and titanate.
perovskite (Fig. 8), but they have a high degree of agglomeration. The small rod like particle is also seen in ZnTiO$_3$ perovskite (See Fig. 8 (c)).

3.2.4 **Infrared spectral studies**

Infrared spectral investigation of these compounds produced an interesting pattern, which seem to be related to the crystal phases. Table VII depicts the infrared spectral data of unsubstituted and substituted perovskite oxides. Three vibrational modes were expected for ABO$_3$ perovskite, $\nu_1$ which is related to the B-O stretch, $\nu_2$ which is assigned to the B-O-B bend, and $\nu_3$ which is related to the A-BO$_3$ lattice mode [60-63]. Some splitting may occur in the case of distorted perovskites, which lead to additional bands [64]. In the present study, the $\nu_1$ vibration was observed at approximately 663 cm$^{-1}$, assigned to the stretching vibration and that at lower frequency $\nu_2 = 547$ cm$^{-1}$ to the bending vibration. It is also observed that substituted perovskite, the band at $\nu_2$ become less defined, most likely due to a smaller distortion of the octahedra.

3.2.5 **Electrical conductivity studies**

Fig. 9 depicts the dependence of log$\sigma$ against the reciprocal temperature ($T^{-1}$) for SrSnO$_3$, SmMnO$_3$, NdAlO$_3$, ZnTiO$_3$ and their respective substituted compounds. The conductivity increases linearly with increasing temperature except four sample showing two district slope with a ‘break’ (See Fig. 9 (b) and (c)). The change in slope is usually expected to happen at the currie temperature or due to the presence of two parallel conductivity mechanism with different activation energies [65]. The Arrhenius plot of all compounds showed linear dependence over entire temperature range studied. The activation energy $E_a$ (eV) has been calculated from the slopes of the line and is tabulated in Table VIII. The values of activation energies suggest that the conduction is due to a characteristic of small polar on hopping transport mechanism which occurs in the perovskite oxide along the metal-oxygen-metal chains [66, 67].
It has been previously stated that the A-site cation disorder reduces the break temperature, Tc \[68\]. It seems that the A-site cation mismatch factor (\(\sigma^2\)) plays a more significant role than the average cation size \(<R_A>\) in all substituted perovskite compounds.

The log \(\sigma\) Vs. \(T^{-1}\) for SrSnO\(_3\) and Sr\(_{0.953}\)Eu\(_{0.047}\)Sn\(_{0.953}\)Co\(_{0.047}\)O\(_3\) (Fig. 9 (a)) showed an initial decrease in electric conductivity in the temperature range 36 to 140\(^\circ\)C, which corresponds to desorption of adsorbed water molecules, usually adsorbed water molecules behave as an electron donor. After 140\(^\circ\)C, the conductivity linearly increases with the temperature for these compounds. This happens in anion deficient phases and the concentration of anion vacancies depends on the synthesis conditions such as temperature and oxygen activity. The conductivity increases with A- and B-sites doping (Fig. 9 (a) and Table VIII) and is comparable to that of electronic conductors based on the perovskite structure \[69\].

Figure 9 (b) shows electrical conductivity as a function of temperature for SmMnO\(_3\) and Sm\(_{0.948}\)Bi\(_{0.052}\)Mn\(_{0.965}\)Cu\(_{0.035}\)O\(_3\) compounds. It is observed that the electrical conductivity (\(\sigma\)) has increased during the substitution in the system. One reason for an increase in the conductivity might be that the substitution of Cu\(^{2+}\) for Mn was compensated electronically by the oxidation of Mn\(^{3+}\) - Mn\(^{4+}\). An increase in the number of Mn\(^{3+}\) - Mn\(^{4+}\) couples would lead to an increased amount of available hopping sites. The greater number of available hopping sites, higher the conductivity values expected. Thus the mixed Mn\(^{3+}\) - Mn\(^{4+}\) could explain the enhanced electronic conductivity \[70\]. In our study, A-site and B-site were substituted with 5 wt. % Bi and 5 wt. % Cu respectively. Thus, the ratio of Mn\(^{3+}\) - Mn\(^{4+}\) is not 1:1 thus indicating a Mn\(^{3+}\) rich rate in Sm\(_{0.948}\)Bi\(_{0.052}\)Mn\(_{0.963}\)Cu\(_{0.035}\)O\(_3\) system. This means that Mn\(^{3+}\)-Mn\(^{4+}\) coupled increased despite the decrease in Mn\(^{3+}\) concentration and the formation oxygen
vacancies at high temperature [71]. Since the formation of oxygen ion vacancies leads to decrease in carrier concentration and carrier mobility [72].

The conductivity of NdAlO$_3$ and Nd$_{0.954}$ Dy$_{0.046}$ Al$_{0.954}$ Fe$_{0.046}$ O$_3$ shows the Arrhenius dependence of the temperature showing two different slopes with kink at ~ 581k (Fig. 9 (c)). At room temperature these materials have high resistance, which may be caused by the large grain boundary contribution to the total resistance. The activation energies were obtained from the slope. The low value of activation energy $E_a$ in Region A, this could be due to defect association. The high value of $E_a$ in the Region B, is due to oxide ion vacancies, and this might be more strongly associated with the dopants.

Fig.9 (d) shows the electrical conductivity vs. reciprocal temperature of ZnTiO$_3$ and Zn$_{0.957}$ Tb$_{0.043}$ Ti$_{0.960}$ Zn$_{0.040}$ O$_3$ compounds. They show semiconductor behavior in the temperature range 80 to 600$^\circ$C. It can be easily interpreted in terms of increase in charge carriers (oxygen vacancy) of these compounds i.e. hopping of small polarons from site to site. Because of the strong interaction of the current carries with the lattice vibration deformation potential at a given site must influence the electrical conductivity.

### 3.2.6 Thermoelectric Power measurement

The effect of temperature on the thermoelectric power for all unsubstituted and substituted perovskites is depicted in Fig. 10. It is noticed that the negative charge carriers for all samples decrease slowly with the temperature up to 400K and then slowly increases as the temperature increases. The negative values of the thermoelectric power confirmed n-type semiconductor in the whole temperature range. This change in semiconductor depends on the nature of both A-site cation and B-site cation in the perovskite structure. In general, (i) bigger A-site cation induces greater reduction stability which are n-type semiconductor. These results indicate that the substituent is an electron donor in the conduction band also creates more vacancies. Here, oxygen
vacancies act as donor’s centers. (ii) secondly, the transition metal ion present at B-site of perovskite, create mixed valent metal ion couples would lead to an increased amount of available hopping sites (i.e. increased electrons) (iii) In stannate have a continuous edge sharing of transition metal ion (i.e. Co$^{2+}$) and Sn$^{4+}$ octahedra is a necessary criterion for the formation of n-type conductivity [73].

3.2.7 Dielectric Studies

Fig. 11 shows the variation of dielectric constant ($\varepsilon'$) as a function of frequency in the range 20 Hz to 200 KHz for unsubstituted and substituted perovskite oxides. All the samples exhibit dielectric dispersion. The value of ($\varepsilon'$) is high at low frequencies, and then it decreases rapidly upto 25 KHz and remains constant afterwards. The observed behavior has been explained by the phenomenon of dipole relaxation, wherein at low frequencies the dipoles are able to follow the frequency of the applied field, where at higher frequency dipole are not able to follow the frequency of the applied field.

Fig. 12 represents the variation of dielectric loss (tan$\delta$) as a function of frequency for all perovskites studied in the present work. It is observed that, the dielectric loss initially decreases and then remain constant. This may be due to the interfacial / space charge polarization effects. In other words, the dielectric loss is inversely proportional to the frequency that causes a reduction of dielectric loss with the increase in frequency [74]. At higher frequencies, these perovskites exhibits a constant dielectric loss behavior, which suggests all samples possess a loss less nature.

3.2.8 Photocatalytic studies

3.2.8.1 Band Gap Measurement

In order to determine the optical energy band gap of the sample, diffuse reflectance UV-vis spectrum (DRS) was recorded (Fig.13). All unsubstituted and substituted perovskite oxides exhibited a typical optical absorption behavior of a wide
band gap semiconductor oxide having an intense absorption band with a steep edge $\lambda$ in nm is given Table IX. The optical absorption near the band edge can be calculated using the relation $E_g = \frac{1200}{\lambda}$, where, $E_g$ is the band gap energy of the photocatalyst in electron volts, and $\lambda$ is absorption edge wavelength in nanometer. The band gap energy, thus obtained for unsubstituted and substituted perovskite oxide summarized in Table IX. These band gap can be attributed to photo excitation of electrons from the valence band to the conduction band. The effect of substitution at A- and B-site of perovskite was also examined using UV-vis-diffuse reflectance spectra. The results showed that absorption edge wavelength ($\lambda$) was red-shifted with the substitution. Obviously their band gap is smaller (See Table IX) than the unsubstituted perovskite oxides. Following Refs. [76, 77] this smaller bandgap was attributed to the introduction of trap center into the band gap.

3.2.8.2 Photodegradation studies on Victoria blue-B and Brilliant yellow solution.

(a) Preliminary experiment

When Victoria blue-B and Brilliant yellow are exposed to sunlight without the catalyst (i.e. perovskite oxide) no significant change in the concentration of these dyes is observed even after 120 min. This reveals that these dyes do not undergo solar photolysis. Victoria blue-B and Brilliant yellow is degraded completely in 150 min in the presence of perovskite oxide and sunlight. Therefore, we have decided to study the various experimental parameters, the photodegradability was tested.

(b) Effect of initial concentration

The initial concentration of dye is also another parameter which needs to be taken into account. The effect of initial concentration of Victoria blue-B and Brilliant yellow solution on the photocatalytic process was examined. The reactions of dye degradation were carried out in the range of 100-300 mg/L for Victoria blue-B and 10-40 mg/L of Brilliant yellow under sunlight. As shown in Fig. 14 (a) and (a’), the
photocatalytic activity of unsubstituted perovskite (50mg) showed a big difference with the initial concentration of these dye solutions varied from 100-300 mg/L. It can be observed that the photocatalytic degradation rate decreases as the initial concentration of these dye solution increases. The degradation rate reached 93.67% when the Victoria blue-B concentration was 100 mg/L and 84.60%, when the Brilliant yellow concentration was 20 mg/L. The photocatalytic degradation of aromatic compounds was related to the formation of hydroxyl radicals \[78\], which were formed by the reaction of holes with adsorbed OH\(^-\) and H\(_2\)O. When the concentration of these dyes increased, the generation of OH\(^-\) radicals would be reduced since there were only fewer sites available for the adsorption of OH\(^-\).

c) Effect of amount of perovskite oxide

The percent degradation rate showed an obvious increase after adding perovskite oxide photocatalyst. The photocatalytic degradation rate was enhanced with the concentration of unsubstituted perovskite oxide called catalyst increasing from 10mg/50ml to 75mg/50ml, with optimum Victoria blue–B (100 mg / L) and Brilliant yellow (20 mg/l) under sunlight, because both the active sites on the catalyst surface and the absorption of light by the catalyst increased with the increase of catalyst quantity. In the beginning, with increasing the amount of the catalyst loading, the surface area of the catalyst increase correspondingly and more light quanta are adsorbed without significant provoking light scattering, leading to the improved photocatalytic degradation. It is observed from Fig. 14 (b) and (b’) that with an increase in the amount of catalyst, the percent degradation of these dyes increases upto 50 mg of catalyst. The maximum of 94% and 85% Victoria blue-B and Brilliant yellow degradation, respectively, are observed, when the amount of 50 mg of catalyst. Further increase in amount, decreases the percent degradation of these dyes. This might be attributed to over-lapping or aggregation of adsorption sites resulting in a decrease in the total
catalyst surface area available to the dye and increase in path length [79]. Thus, any further increase in the amount of the catalyst will make more decreasing effect on the percent photodegradation [80].

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

The pH values appear to play an important role in the photocatalytic process of various dyes [81, 82]. The influence of the initial pH value, ranging between 2.0 to 10.0, on the percent photodegradation of Victoria blue-B (100mg/L) and Brilliant yellow (20 mg/L) for the 50 mg unsubstituted perovskite oxide suspensions with sunlight irradiation time 120 min is investigated as shown in Fig. 14 (c) and (c’).

In the illuminated unsubstituted perovskite oxide system, the percent degradation of the Victoria blue-B is higher at alkaline pH values with a more than twofold increase as pH increases from 2.5 to 7.5. At pH 7.5, the maximum percent degradation is achieved. And with the further increase of the pH values, the percent photodegradation of these dyes turns low gradually. The observed trends are clearly correlated to the electrostatic interaction between these dyes and photocatalyst surface, depending on the pH of the suspension [83].

e) **Effect of contact time**

The plot of experimentally derived values of percent degradation vs. time for unsubstituted and substituted perovskite oxide is described in Fig. 15 (a). The degradation of Victoria blue-B and Brilliant yellow, which was catalyzed by these perovskite oxides under sunlight irradiation. The rate of percent degradation is initially quite rapid with most of the unsubstituted and substituted perovskite oxides within first 90 minutes; thereafter the percent degradation was found to be slow. It is basically due to saturation of the active site which does not allow further adsorption to take place for degradation of the dye [84].
Alig et al. [85, 86] has reported that the direct absorption of photons by the band gap of the perovskite oxides can generate electron-hole pairs in the solid, but the requirement of energy is generally higher than the band gap of the perovskite oxides. Usually, two possible approaches could be adopted to enhance the activity of these catalysts. One way could be to increase the sunlight irradiation energy. The other could be to further modify the catalyst to increase the range of wavelengths at which the catalyst is active. As shown in Table IX, the percent degradation of Victoria blue-B and Brilliant yellow exhibits the stannate (SrSnO$_3$; Sr$_{0.953}$ Eu$_{0.047}$ Sn$_{0.953}$ Co$_{0.047}$ O$_3$) and titanate (ZnTiO$_3$; Zn$_{0.957}$ Tb$_{0.043}$ Ti$_{0.960}$ Zr$_{0.040}$O$_3$) have higher photocatalytic performance than that of manganate (SmMnO$_3$; Sm$_{0.948}$ Bi$_{0.052}$ Mn$_{0.965}$ Cu$_{0.035}$ O$_3$) and aluminate (NdAlO$_3$; Nd$_{0.954}$ Dy$_{0.046}$ Al$_{0.954}$ Fe$_{0.046}$ O$_3$). However, the percent degradation of Victoria blue-B showed higher values as compared to Brilliant yellow dye (See Table IX).

It is also interesting to observe that the percent degradation of these dyes showed slightly higher values by using substituted perovskite as compared to unsubstituted perovskite oxide catalyst.

It is known that the substituted metal ion serves as an electron (e$^-$) donor and prohibits the recombination of holes (h$^+$) and electron (e$^-$) pairs at low concentration. In addition, there are other reasons as follows. The substitution of metal ions in to B-site of perovskite type oxide there is likely to form, oxygen vacancy due to charge compensation phenomenon. Hence substituted perovskite oxide exhibits an enhanced redox reaction ability for degradation of dyes.

Finally, the substitution of metal ion at B-site of BO$_6$ octahedral, thus leading to the change of bond angle and bond length. On the other hand, M-O binding energy will decrease. It is favorable for the formation of more oxygen vacancy traps on the surface of the photocatalytic activity of substituted perovskite, can be greatly improved.
However, the photocatalytic activity declines with the further increase of substituting amount. The reason is that the large substituting amount is more likely to serve as recombination centers than as trap sites for charge transfer at the interface. So, there is an optimum metal ion substitution for highest photocatalytic activity.

It is generally believed that in perovskite type oxides (ABO$_3$) A-site cations are catalytically inert components whose effect on photocatalytic process is negligibly small compared to that of B-site cation which are the catalytically active centers, because the conduction band and the valence band mainly consist of d orbitals and p orbitals respectively[87, 88]. A-Site cation of perovskite type oxide also affect the photocatalytic activity and that partly occupied 4f-level of the lanthanides may have a key role in photocatalytic reaction [89-92].

f) Photodegradation kinetics

The photocatalytic degradation generally follows a Langumuir Hinesh wood mechanism [93]. From Fig.15 (a), it can be clearly seen Victoria blue-B and Brilliant yellow were degraded fast by unsubstituted and substituted perovskite oxides under sunlight irradiation. The rate constant (k, min$^{-1}$) for the photodegradation reaction of these dye is determined by the following relation; ln (Co/C) = 1 where Co and C denote the dye concentration at t=0 and t=t, respectively. The k value was calculated from the slope between ln (Co/C) and time (t). It indicates that the degradation reaction can be expressed by the pseudo first order reaction kinetic model and the rate constants are depicted in Table IX. It is observed that the rate constant (k) for Victoria blue-B show higher value than the Brilliant yellow by using unsubstituted and substituted perovskite oxide photo catalyst. It also observed that the rate constant (k) is slightly increased in case of all substituted perovskite oxides.
g) **Measurement of Chemical oxygen demand (COD)**

The measurement of the chemical oxygen demand (COD) of the irradiated Victoria blue–B and Brilliant yellow solution by using unsubstituted and substituted perovskite oxides as photocatalyst are generally used for monitoring the mineralization of the dye. To determine the COD removal in all perovskite type oxides sensitized photooxidation, these dye samples were tested as follows. Reaction conditions included: concentration of dyes = 100mg/L for Victoria blue –B at pH= 7.5 and 20 mg/L for Brilliant yellow at pH=2.5, the amount of perovskite-type oxide = 50 mg, under sunlight irradiation over 2 hrs. and then these samples were collected during the test for COD determination. The results are summarized in Table IX. From the results, it was found that COD decreases after photooxidation.

h) **Mechanism of Photodegradation**

Generally, the effect of pH value on the photocatalytic reaction is attributed to the surface absorption of the catalyst and relation with the ionic form of the dye compound (anionic or cationic dye). Electrostatic attraction or repulsion between the catalyst surface and the dye molecule take place, and the photodegradation rate is consequently enhanced or inhibited, respectively. Since, the Victoria blue-B is an ionizable compound, the increase of the degradation at alkaline pH can be described to the high hydroxylation of the catalyst surface due to the presence of a large quantity OH⁻ ions. Although at higher alkali pH, the electrostatic attraction is improved, and the hydroxyl group on the surface of catalyst decrease simultaneously due to the breakage of the hydroxylation of the catalyst surface. This leads to the decline of % photodegradation at pH > 8. Consequently, there exists an optimum pH value of 7.5 for photodegradation of Victoria blue–B on the unsubstituted and substituted perovskite oxide catalyst surface.
Under acidic condition, it is difficult to cationic Brilliant yellow dye to adsorb onto the perovskite oxide surface. This is because, as the initial pH of this dye solution decreased, the number of negatively charged catalyst sites decreased and positively charged sites increased which did not favor the adsorption, since Brilliant yellow is a cationic dye resulting in electrostatic repulsion. This decrease in the adsorption at lower pH = 2.5 is also due to the fact that the presence of excess H\(^+\) released from the Brilliant yellow dye at acidic condition which opposing with dye cations for the adsorption. Therefore, the percent degradation of this dye slightly less than Victoria blue-B dye.

The photocatalysis of unsubstituted and substituted perovskite oxides, we concluded that (a) These catalysts (perovskite powder) serve as electron and hole sources for degradation of Victoria blue –B and Brilliant yellow under sunlight irradiation. (b) The relationship between the crystal structure and photocatalytic performance in the photochemical degradation of these dyes are close knit. We have observed that the photocatalytic activity of cubic and hexagonal phase of stannate and titanate perovskite type oxides respectively, have much higher percent degradation of these dyes than the orthorhombic phase of remaining perovskite oxides (i.e. manganate and aluminate). (c) The photocatalytic activity parameter such as catalyst amount and pH values also plays an important role in tuning the photocatalytic performance.

The photocatalytic behavior can be understood by considering the possible mechanisms of dye photodegradation, i.e. the direct and indirect mechanisms,[94-99]. When a perovskite type oxidewith appropriate band gap energy is irradiated with sunlight electron are excited into the conduction band (e\(^-\text{CB}\)) and holes are formed in the valence band (h\(^+\text{VB}\)). According to the direct mechanism these photogenerated electrons may interact with the Victoria blue-B or Brillinet yellow dye adsorbed into the surface of a perovskite oxide, thereby leading to the formation R\(^+\) and then to its degradation.
These electrons may also interact with the acceptor molecule such as O₂ adsorbed on the surface of perovskite oxide or dissolved in water, thereby leading to the formation of a superoxide. According to the indirect mechanism, the photogenerated holes may oxidize species such as OH⁻ or H₂O, thereby forming OH free radicals, which are a strong oxidizing agent that can react with the dyes. The major initial steps in the mechanism under sunlight are summarized by:

Perovskite type oxide (ABO₃) + hν \rightarrow e⁻_{CB} + h⁺_{VB}

e⁻_{CB} + O₂ \rightarrow O₂⁻

O₂⁻ + H₃O⁺ \rightarrow OH + HO₂ + H₂O₂

h⁺_{VB} + H₂O (OH) \rightarrow OH + H⁺

OH or h⁺_{VB} + dye \rightarrow degradation

i) Efficiency of reused perovskite type oxide

Unsubstituted and substituted perovskite oxides used in the treatment was centrifuged, and desorption of dye was done using chemical leaching method. HCl (0.1N) was used to desorbs the dye (Victoria blue-B or Brilliant yellow) from the perovskite type oxide adsorbent and dried at 150°C in a hot oven before it was reused for the succeeding photocatalytic degradation experiments. However, the results obtained, for regenerated catalyst were not so significant and the perovskite type oxide (ABO₃) shows poor adsorption efficiency after first use. So, it cannot be recycled and reused, further as a catalyst for Victoria blue–B or Brilliant yellow in aqueous solution.

4. Conclusions

a) The unsubstituted and substituted perovskite-type compounds such as, SrSnO₃, Sr₀.₉₅₃Eu₀.₀₄₇Sn₀.₉₅₃Co₀.₄₇₇O₃; SmMnO₃, Sm₀.₉₄₈Bi₀.₀₅₂Mn₀.₉₆₅Cu₀.₀₃₅O₃; NdAlO₃, Nd₀.₉₅₄Dy₀.₀₄₆Al₀.₉₅₄Fe₀.₀₄₆O₃; ZnTiO₃, Zn₀.₉₅₇Tb₀.₀₄₃Ti₀.₉₆₀Zr₀.₀₄₀O₃ are synthesized by tartarate and hydroxide precursor method.
b) The X-ray diffraction pattern of single phase perovskite such as SrSnO$_3$, Sr$_{0.953}$Eu$_{0.047}$Sn$_{0.953}$Co$_{0.047}$O$_3$; SmMnO$_3$, Sm$_{0.948}$Bi$_{0.052}$Mn$_{0.965}$Cu$_{0.035}$O$_3$; NdAlO$_3$, Nd$_{0.954}$ Dy$_{0.046}$Al$_{0.954}$Fe$_{0.046}$O$_3$ are found cubic structure, while SmMnO$_3$ and Sm$_{0.948}$ Bi$_{0.052}$ Mn$_{0.965}$ Cu$_{0.035}$ O$_3$ is orthorhombic; and ZnTiO$_3$, Zn$_{0.0957}$ Tb$_{0.043}$Ti$_{0.0960}$Zr$_{0.040}$O$_3$ is hexagonal structure.

c) The lattice parameter and unit cell volume for all perovskite compounds are not change except SmMnO$_3$, Sm$_{0.948}$Bi$_{0.052}$Mn$_{0.965}$Cu$_{0.035}$O$_3$. Because at B-site, substituting Cu$^{2+}$ will lead to an expansion of the unit cell volume rather than a contraction when A-site doped by smaller cation ions as well as at B-site doping, average size of cations $<R_A>$, mismatch factor ($\sigma^2$) and tolerance factor (t) gives the combine information about the structural changes from perfect cubic to less symmetric orthorhombic or hexagonal structure.

d) The particulate properties like X-ray density and apparent density increase at A-site and B-site substitution of perovskite, while corresponding porosity value decreases. The average particle size determined from scanning electron micrographs (SEM) are found in the range of 22.14 nm to 70.19 nm, which indicate the nanosized particles.

e) The temperature dependence of the electrical conductivity for all compounds showed a semiconducting behavior. The activation energy (Ea) in the first region corresponds to the charge carriers are localized on the defect center, while activation energy (Ea) in the second region corresponds to an intrinsic semiconductor of all perovskite oxides.

f) Thermoelectric power measurement showed all compounds are n-type semiconductor.

g) The variation of dielectric constant ($\varepsilon'$) and dielectric loss (tan$\delta$) with the frequency for all perovskite oxides suggest the dipole relaxation phenomenon.
h) The photocatalytic degradation of Victoria blue-B and Brilliant yellow over unsubstituted and substituted perovskite oxides under sunlight was investigated. The processing parameters such as the initial concentration of Victoria blue-B (100mg/L) at pH=7.5 and Brilliant yellow (20 mg/L) at pH=2.5 and the amount of perovskite (50 mg) also play an important role in tuning the photocatalytic activity. The percent degradation of Victoria blue-B and Brilliant yellow exhibits stannate and titanate and their substituted compounds have higher photocatalytic performance than that of magnates and aluminate perovskite type oxides. Pseudo first order rate constant (k) is slightly increased in case of all substituted perovskite oxides. Chemical oxygen demand (COD) is used for monitoring the mineralization of above dye.
5. References

46. JCPDS File No.22-1442
47. JCPDS File No.25-0747
48. JCPDS File No.29-0056
49. JCPDS File No.14-0033


**Table I:** Observed elemental and XRF data of precursor

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Precursor</th>
<th>Formula wt.</th>
<th>Elemental analysis in wt % (±0.5)</th>
</tr>
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<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Req</td>
</tr>
<tr>
<td>Strontium-stannate hydroxide hydrate</td>
<td>SrSn(OH)$_6$.0.5$\text{H}_2\text{O}$</td>
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<tr>
<td>Samarium-manganese tartarate dihydrate</td>
<td>SmMn(C$_4$H$_4$O$<em>6$)$</em>{2.5}$.2$\text{H}_2\text{O}$</td>
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<td>19.64</td>
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<tr>
<td>Neodymium-aluminium tartarate dihydrate</td>
<td>(NH$_4$)$_2$<a href="OH">NdAl(C$_4$H$_4$O$_6$)$_4$</a>$_2$.2$\text{H}_2\text{O}$</td>
<td>869.65</td>
<td>22.09</td>
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<td>Zinc-titanium tartarate hydrate</td>
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<td>510.39</td>
<td>23.51</td>
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</table>

**Note:** The values in the table represent the observed elemental analysis of the precursors. The columns indicate the required (Req) and found (Found) percentages for carbon (C) and hydrogen (H) as well as the metal elements (Sr, Sm, Nd, Al, Zn, Ti).
**Table II**: Infrared spectral bands and their probable assignments for tartarate / hydroxide precursor

<table>
<thead>
<tr>
<th>Bands for cm⁻¹</th>
<th>Bands for cm⁻¹</th>
<th>Bands for cm⁻¹</th>
<th>Bands for cm⁻¹</th>
<th>Assignments</th>
</tr>
</thead>
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<tr>
<td>SrSn(OH)₆, 0.5H₂O</td>
<td>SmMn(C₆H₄O₂)₂.25·2H₂O</td>
<td>(NH₄)₂[NdAl(C₆H₄O₂)₄(OH)]₂</td>
<td>ZnTi(C₆H₄O₂)₂.5·1.5H₂O</td>
<td>Assignments</td>
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<td>3338(s)</td>
<td>3396(m)</td>
<td>3306(m)</td>
<td>3433(m)</td>
<td>υ stretching HOH</td>
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<tr>
<td>1622(m)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>υ Sn-OH (in plane deformed)</td>
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<td>-</td>
<td>1562(s)</td>
<td>1599(s)</td>
<td>1589(s)</td>
<td>υ asy (C = O)</td>
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<td>1404(s)</td>
<td>-</td>
<td>υ NH₄⁺</td>
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<td>-</td>
<td>1367(s)</td>
<td>1344(s)</td>
<td>1363(m)</td>
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<tr>
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<td>1303(w)</td>
<td>1305(w)</td>
<td>υ (C – C)</td>
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<td>-</td>
<td>1215(m)</td>
<td>-</td>
<td>υ N-OH</td>
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<td>1232(w)</td>
<td>1263(m)</td>
<td>1240(w)</td>
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<td>1099(w)</td>
<td>υ asy C = O</td>
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<td>1004(m)</td>
<td>1051(m)</td>
<td>υ C - O (alcohol)</td>
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<td>927(w)</td>
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<tr>
<td>-</td>
<td>881(w)</td>
<td>893(s)</td>
<td>893(w)</td>
<td>υ asy (C – O), δ (O – C – O)</td>
</tr>
<tr>
<td>856(w)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>υ Sn-OH (deformed)</td>
</tr>
<tr>
<td>-</td>
<td>839(w)</td>
<td>833(w)</td>
<td>831(w)</td>
<td>υ C - H wag</td>
</tr>
<tr>
<td>-</td>
<td>715(m)</td>
<td>702(w)</td>
<td>736(w)</td>
<td>υ₃ C – C</td>
</tr>
<tr>
<td>665 (m)</td>
<td>569(w)</td>
<td>642(w)</td>
<td>640(m)</td>
<td>υ M – O</td>
</tr>
<tr>
<td>538(s)</td>
<td>532(m)</td>
<td>549(m)</td>
<td>538(m)</td>
<td>υ(m – o), υ(C – C)</td>
</tr>
</tbody>
</table>

(s = strong, 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>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% mass loss</td>
<td>Temp. range (°C)</td>
<td>Obsd.</td>
</tr>
<tr>
<td>SrSn(OH)$_6$.0.5$\text{H}_2\text{O}$</td>
<td>2.54</td>
<td>2.83</td>
<td>50 - 140</td>
</tr>
<tr>
<td>SmMn (C$_4$H$_4$O$_6$)$_2$.5$.2$H$_2$O</td>
<td>5.55</td>
<td>5.88</td>
<td>30 - 150</td>
</tr>
<tr>
<td>(NH$_4$)$_2$[NdAl (C$_4$H$_4$O$_6$)$_4$(OH)$_2$].2$\text{H}_2\text{O}$</td>
<td>4.24</td>
<td>4.13</td>
<td>30 - 100</td>
</tr>
<tr>
<td></td>
<td>78.32</td>
<td>76.88</td>
<td>240 - 750</td>
</tr>
<tr>
<td>ZnTi (C$_4$H$_4$O$<em>6$)$</em>{2.5}$.1.5$\text{H}_2\text{O}$</td>
<td>4.78</td>
<td>5.29</td>
<td>30 - 150</td>
</tr>
</tbody>
</table>
Table IV: Observed XRF and EDAX analysis of undoped and doped nanocrystalline perovskites

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Metal analysis in wt % (±0.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sr</td>
</tr>
<tr>
<td>SrSnO₃</td>
<td>34.45</td>
</tr>
<tr>
<td>Sr₀.₉₅₃Eu₀.₀₄₇Sn₀.₉₅₃Co₀.₀₄₇O₃</td>
<td>32.80</td>
</tr>
<tr>
<td></td>
<td>Sm</td>
</tr>
<tr>
<td>SmMnO₃</td>
<td>59.36</td>
</tr>
<tr>
<td>Sm₀.₉₄₈Bi₀.₀₅₂Mn₀.₉₆₅Cu₀.₀₃₅O₃</td>
<td>55.57</td>
</tr>
<tr>
<td></td>
<td>Nd</td>
</tr>
<tr>
<td>NdAlO₃</td>
<td>65.79</td>
</tr>
<tr>
<td>Nd₀.₉₅₄Dy₀.₀₄₆Al₀.₀₄₆Fe₀.₀₄₆O₃</td>
<td>62.15</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
</tr>
<tr>
<td>ZnTiO₃</td>
<td>40.54</td>
</tr>
<tr>
<td>Zn₀.₉₅₇Tb₀.₀₄₃Ti₀.₉₆₀Zr₀.₀₄₀O₃</td>
<td>37.46</td>
</tr>
</tbody>
</table>

* The figures in parenthesis indicate metal analysis obtained from EDAX method.
**Table V:** X-ray diffraction data of undoped and doped perovskite oxides

<table>
<thead>
<tr>
<th></th>
<th>SrSnO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Sr&lt;sub&gt;0.953&lt;/sub&gt;Eu&lt;sub&gt;0.047&lt;/sub&gt;Sn&lt;sub&gt;0.953&lt;/sub&gt;Co&lt;sub&gt;0.047&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>SmMnO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Sm&lt;sub&gt;0.948&lt;/sub&gt;Bi&lt;sub&gt;0.052&lt;/sub&gt;Mn&lt;sub&gt;0.965&lt;/sub&gt;Cu&lt;sub&gt;0.035&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>NdAlO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Nd&lt;sub&gt;0.954&lt;/sub&gt;Dy&lt;sub&gt;0.046&lt;/sub&gt;Al&lt;sub&gt;0.954&lt;/sub&gt;Fe&lt;sub&gt;0.046&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>ZnTiO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Zn&lt;sub&gt;0.95&lt;/sub&gt;Tb&lt;sub&gt;0.043&lt;/sub&gt;Ti&lt;sub&gt;0.960&lt;/sub&gt;Zr&lt;sub&gt;0.040&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0405(9)*</td>
<td>4.0333(9)*</td>
<td>3.4875 (17)*</td>
<td>3.4715 (15)*</td>
<td>3.7604(54)*</td>
<td>3.754 (53)*</td>
<td>2.7911(100)*</td>
<td>2.7911(100)*</td>
<td></td>
</tr>
<tr>
<td>2.8572(100)</td>
<td>2.8572 (100)</td>
<td>2.9247 (16)</td>
<td>2.9684 (8)</td>
<td>2.6589 (100)</td>
<td>2.652 (100)</td>
<td>2.5391 (13)</td>
<td>2.4584 (97)</td>
<td></td>
</tr>
<tr>
<td>2.0197 (39)</td>
<td>2.0214 (20)</td>
<td>2.7153 (100)</td>
<td>2.7153 (100)</td>
<td>2.1731 (40)</td>
<td>2.1692 (41)</td>
<td>2.3528 (9)</td>
<td>2.3528 (9)</td>
<td></td>
</tr>
<tr>
<td>1.8058 (3)</td>
<td>1.8153 (5)</td>
<td>2.6759 (32)</td>
<td>2.6994 (10)</td>
<td>2.1612 (24)</td>
<td>2.0971 (8)</td>
<td>2.3434(6)</td>
<td>2.3434(6)</td>
<td></td>
</tr>
<tr>
<td>1.6489 (33)</td>
<td>1.6489 (22)</td>
<td>2.1792 (17)</td>
<td>2.1812 (19)</td>
<td>1.8894(18)</td>
<td>1.8776(37)</td>
<td>2.2318 (13)</td>
<td>2.2318 (3)</td>
<td></td>
</tr>
<tr>
<td>1.4250 (5)</td>
<td>1.4266 (10)</td>
<td>1.9730 (9)</td>
<td>1.9910 (29)</td>
<td>1.6846 (16)</td>
<td>1.6886 (12)</td>
<td>2.1701 (14)</td>
<td>2.1701 (4)</td>
<td></td>
</tr>
<tr>
<td>1.2776 (10)</td>
<td>1.2770 (10)</td>
<td>1.902 (11)</td>
<td>1.9103 (9)</td>
<td>1.5355 (30)</td>
<td>1.5359 (26)</td>
<td>1.6190 (41)</td>
<td>1.6190 (41)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.8762 (11)</td>
<td>1.8762 (19)</td>
<td>1.3314(3)</td>
<td>1.333(10)</td>
<td>1.4692 (9)</td>
<td>1.4734 (24)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5509 (18)</td>
<td>1.5528 (23)</td>
<td>1.2514 (8)</td>
<td>1.2528(9)</td>
<td>1.3692 (13)</td>
<td>1.3743 (23)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4317 (11)</td>
<td>1.4589 (14)</td>
<td></td>
<td></td>
<td>1.2357 (4)</td>
<td>1.2357 (4)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The figures in parenthesis are intensities relative to the line of highest intensity (100%)*
### Table VI: Structural data of undoped and doped perovskite compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Structure</th>
<th>Lattice constant 'a' nm</th>
<th>Unit cell volume*divided by Z (nm)^3</th>
<th>Average cation sizes of A site of perovskite &lt;R_A&gt;Å</th>
<th>Average cation sizes of A site of perovskite &lt;R_B&gt;Å</th>
<th>Mismatch factor σ^2 (Å)^2</th>
<th>Tolerance factor (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrSnO₃</td>
<td>Cubic</td>
<td>0.807</td>
<td>0.526</td>
<td>1.310</td>
<td>0.810</td>
<td>0.000</td>
<td>0.867</td>
</tr>
<tr>
<td>Sr₀.₉₅₃Eu₀.₄₇Sn₀.₉₅₃Co₀.₄₇O₃</td>
<td></td>
<td>0.807</td>
<td>0.526</td>
<td>1.301</td>
<td>0.804</td>
<td>2.840 x 10^-3</td>
<td>0.866</td>
</tr>
<tr>
<td>SmMnO₃</td>
<td>Orthorhombic</td>
<td>a=0.534</td>
<td>b=0.582</td>
<td>c=0.748</td>
<td>0.233</td>
<td>1.132</td>
<td>0.580</td>
</tr>
<tr>
<td>Sm₀.₉₄₈Bi₀.₀₅₂Mn₀.₉₆₅Cu₀.₃₅O₃</td>
<td>Orthorhombic</td>
<td>a=0.531</td>
<td>b=0.588</td>
<td>c=0.751</td>
<td>0.234</td>
<td>1.134</td>
<td>0.585</td>
</tr>
<tr>
<td>NdAlO₃</td>
<td>Cubic</td>
<td>0.376</td>
<td>0.053</td>
<td>1.163</td>
<td>0.535</td>
<td>0.000</td>
<td>0.937</td>
</tr>
<tr>
<td>Nd₀.₉₅₄Dy₀.₀₄₆Al₀.₉₅₄Fe₀.₄₆O₃</td>
<td>Cubic</td>
<td>0.376</td>
<td>0.053</td>
<td>1.159</td>
<td>0.546</td>
<td>3.336 x 10^-4</td>
<td>0.930</td>
</tr>
<tr>
<td>ZnTiO₃</td>
<td>Hexagonal</td>
<td>a =0.519</td>
<td>c = 1.375</td>
<td>0.964</td>
<td>0.900</td>
<td>0.740</td>
<td>0.000</td>
</tr>
<tr>
<td>Zn₀.₉₅₇Tb₀.₀₄₃Ti₀.₉₆₀Zr₀.₀₄₀O₃</td>
<td>Hexagonal</td>
<td>a=0.498</td>
<td>c=1.500</td>
<td>0.967</td>
<td>0.908</td>
<td>0.744</td>
<td>1.728 x 10^-3</td>
</tr>
</tbody>
</table>

*Z is 1 in cubic space group, 6 in the hexagonal space group and 4 for the orthorhombic space group
Table VII: Particulate properties and infrared spectral data of substituted perovskite-type nanooxides

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mean crystallite size &lt;D&gt;_{X-Ray} nm ±10%</th>
<th>Surface area (m²/g)</th>
<th>X-Ray density D_x (g.cm⁻³)</th>
<th>Apparent density D (g.cm⁻³)</th>
<th>Porosity P=1- D/D_x</th>
<th>Average particle size (from SEM) nm</th>
<th>Infrared spectral absorption band cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrSnO₃</td>
<td>43.45</td>
<td>19.15</td>
<td>6.412</td>
<td>1.492</td>
<td>0.767</td>
<td>70.19</td>
<td>ν₁ 663</td>
</tr>
<tr>
<td>Sr₀.₉₅₃Eu₀.₀₄₇Sn₀.₉₅₃Co₀.₀₄₇O₃</td>
<td>36.8</td>
<td>26.67</td>
<td>6.418</td>
<td>1.008</td>
<td>0.842</td>
<td>38.20</td>
<td>ν₁ 669 ν₂ 532 ν₃ 430</td>
</tr>
<tr>
<td>SmMnO₃</td>
<td>37.95</td>
<td>9.48</td>
<td>7.216</td>
<td>1.456</td>
<td>0.798</td>
<td>68.79</td>
<td>ν₁ 640 ν₂ 538 ν₃ 482</td>
</tr>
<tr>
<td>Sm₀.₉₄₈Bi₀.₀₅₂Mn₀.₉₆₅Cu₀.₀₃₅O₃</td>
<td>41.94</td>
<td>7.63</td>
<td>7.256</td>
<td>1.654</td>
<td>0.772</td>
<td>49.13</td>
<td>ν₁ 638 ν₂ 565 ν₃ 459</td>
</tr>
<tr>
<td>NdAlO₃</td>
<td>43.89</td>
<td>1.02</td>
<td>54.614</td>
<td>0.847</td>
<td>0.984</td>
<td>23.23</td>
<td>ν₁ 696 ν₂ 526 ν₃ 441</td>
</tr>
<tr>
<td>Nd₀.₉₅₄Dy₀.₀₄₆Al₀.₉₅₄Fe₀.₀₄₀O₃</td>
<td>40.98</td>
<td>1.16</td>
<td>55.347</td>
<td>0.963</td>
<td>0.982</td>
<td>22.14</td>
<td>ν₁ 669 ν₂ 500 ν₃ 422</td>
</tr>
<tr>
<td>ZnTiO₃</td>
<td>60.25</td>
<td>59.75</td>
<td>5.550</td>
<td>0.916</td>
<td>0.834</td>
<td>47.42</td>
<td>ν₁ 690 ν₂ 557 ν₃ 440</td>
</tr>
<tr>
<td>Zn₀.₉₅₇Tb₀.₀₄₃Ti₀.₉₆₅Zr₀.₀₄₀O₃</td>
<td>42.59</td>
<td>81.86</td>
<td>5.768</td>
<td>1.126</td>
<td>0.804</td>
<td>36.94</td>
<td>ν₁ 692 ν₂ 542 ν₃ 471</td>
</tr>
</tbody>
</table>
**Table VIII**: Electrical conductivity data and dielectric properties of undoped and doped nanocrystalline perovskites

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Conductivity measurements</th>
<th>Thermoelectric power measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Region</td>
<td>Temp. range (K)</td>
</tr>
<tr>
<td>SrSnO$_3$</td>
<td>A</td>
<td>303 - 806</td>
</tr>
<tr>
<td>Sr$<em>{0.953}$Eu$</em>{0.047}$Sn$<em>{0.953}$Co$</em>{0.047}$O$_3$</td>
<td>A</td>
<td>303 - 877</td>
</tr>
<tr>
<td>SmMnO$_3$</td>
<td>A</td>
<td>308 - 454</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>454- 833</td>
</tr>
<tr>
<td>Sm$<em>{0.948}$Bi$</em>{0.052}$Mn$<em>{0.965}$Cu$</em>{0.035}$O$_3$</td>
<td>A</td>
<td>322 - 471</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>471- 714</td>
</tr>
<tr>
<td>NdAlO$_3$</td>
<td>A</td>
<td>318 - 649</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>649- 925</td>
</tr>
<tr>
<td>Nd$<em>{0.954}$Dy$</em>{0.046}$Al$<em>{0.954}$Fe$</em>{0.046}$O$_3$</td>
<td>A</td>
<td>333 - 581</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>581 - 833</td>
</tr>
<tr>
<td>ZnTiO$_3$</td>
<td>A</td>
<td>308 - 961</td>
</tr>
<tr>
<td>Zn$<em>{0.957}$Tb$</em>{0.043}$Ti$<em>{0.960}$Zr$</em>{0.040}$O$_3$</td>
<td>A</td>
<td>301 – 833</td>
</tr>
</tbody>
</table>
Table IX: Photocatalytic details of undoped and doped nanocrystalline perovskites

<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>SrSnO₃</td>
<td>310</td>
<td>4.00</td>
<td>98.33</td>
<td>81.78</td>
<td>0.034</td>
</tr>
<tr>
<td>Sr₀.₉₅₃Eu₀.₀₄₇Sn₀.₉₅₃Co₀.₀₄₇O₃</td>
<td>466</td>
<td>2.66</td>
<td>98.49</td>
<td>88.79</td>
<td>0.034</td>
</tr>
<tr>
<td>SmMnO₃</td>
<td>300</td>
<td>4.12</td>
<td>55.25</td>
<td>40.55</td>
<td>0.006</td>
</tr>
<tr>
<td>Sm₀.₉₄₅Bi₀.₀₅₂Mn₀.₉₆₅Cu₀.₀₃₅O₃</td>
<td>385</td>
<td>3.22</td>
<td>62.03</td>
<td>47.96</td>
<td>0.008</td>
</tr>
<tr>
<td>NdAlO₃</td>
<td>278</td>
<td>4.45</td>
<td>71.22</td>
<td>48.28</td>
<td>0.010</td>
</tr>
<tr>
<td>Nd₀.₉₅₄Dy₀.₀₄₆Al₀.₉₅₄Fe₀.₀₄₆O₃</td>
<td>367</td>
<td>3.37</td>
<td>73.41</td>
<td>56.70</td>
<td>0.011</td>
</tr>
<tr>
<td>ZnTiO₃</td>
<td>365</td>
<td>3.39</td>
<td>93.67</td>
<td>84.60</td>
<td>0.023</td>
</tr>
<tr>
<td>Zn₀.₉₅₇Tb₀.₀₄₃Ti₀.₉₆₀Zr₀.₀₄₀O₃</td>
<td>379</td>
<td>3.27</td>
<td>97.40</td>
<td>85.73</td>
<td>0.040</td>
</tr>
</tbody>
</table>

VBB- Victoria blue-B , BY-Brilliant yellow
Mixed metal tartarate coprecipitate (i.e. precursors)  
Calcined at 800°C in static air atmosphere for 2 hrs. reground and recalcined at the same temperature  
SmMnO₃  
(Similar procedure is used for doped perovskites)  
Fig. 1: Flowchart for the preparation of nanocrystalline perovskites samarium manganese by tartarate precursor.
Fig. 2: Infrared spectra for precursor
(a) SrSn(OH)$_6$.0.5$H_2$O, (b) SmMn(C$_4$H$_4$O$_6$)$_2.5$. 2$H_2$O
(c) (NH$_4$)$_2$[NdAl(C$_4$H$_4$O$_6$)$_4$(OH)$_2$].2$H_2$O, (d) ZnTi(C$_4$H$_4$O$_6$)$_2.5$.1.5$H_2$O
Fig. 3: TGA and DTA curves for dicarboxylate precursor in normal air atmosphere.
(a) SrSn(OH)$_6$.0.5H$_2$O, (b) SmMn(C$_4$H$_4$O$_6$)$_2$.5H$_2$O
(c) (NH$_4$)$_2$[NdAl(C$_4$H$_4$O$_6$)$_4$(OH)$_2$].2H$_2$O, (d) ZnTi(C$_4$H$_4$O$_6$)$_2$.5.1.5H$_2$O
Fig. 4: Energy dispersive X-ray spectrum (EDAX) of undoped and doped nanocrystalline perovskites 
(a) SrSnO₃, (b) Sr₀.95₃ Eu₀.04₇ Sn₀.95₃ Co₀.0₄₇ O₃, (c) SmMnO₃, (d) Sm₀.₉₄₈ Bi₀.₀₅₂ Mn₀.₉₆₅ Cu₀.₀₃₅ O₃.
Fig. 5: Energy dispersive X-ray spectrum (EDAX) of undoped and doped nanocrystalline perovskites
(a) NdAlO$_3$, (b) Nd$_{0.954}$Dy$_{0.046}$Al$_{0.954}$Fe$_{0.046}$O$_3$, (c) ZnTiO$_3$, (d) Zn$_{0.957}$Tb$_{0.043}$Ti$_{0.960}$Zr$_{0.040}$O$_3$. 
Fig. 6: X-ray diffraction patterns of undoped and doped nanocrystalline perovskites
Fig. 7: Scanning electron micrographs (SEM) of undoped and doped nanocrystalline perovskites.  
(a) SrSnO₃,  (b) Sr₀.₉₅₃Eu₀.₀₄₇Sn₀.₉₅₃Co₀.₀₄₇O₃,  (c) SmMnO₃,  (d) Sm₀.₉₄₈Bi₀.₀₅₂Mn₀.₉₆₅Cu₀.₀₃₅O₃.
Fig. 8: Scanning electron micrographs (SEM) of undoped and doped nanocrystalline perovskites (a) NdAlO$_3$, (b) Nd$_{0.954}$Dy$_{0.046}$Al$_{0.954}$Fe$_{0.046}$O$_3$, (c) ZnTiO$_3$, (d) Zn$_{0.957}$Tb$_{0.043}$Ti$_{0.960}$Zr$_{0.040}$O$_3$.
Fig. 9: Plot of log $\sigma$ against $T^{-1}$ of undoped and doped nanocrystalline perovskites
Fig. 10: Plot of thermoelectric power, $\mu$ (volt k$^{-1}$) against temperature (K) for (a) Undoped (b) doped nanocrystalline perovskites
Fig. 11: Plot of variation of dielectric constant ($\varepsilon'$) with frequency for (a) undoped and (b) doped Nanocrystalline perovskites.
Fig. 12: Plot of variation of dielectric loss (\(\tan \delta\)) with frequency for (a) undoped and (b) doped nanocrystalline perovskites
Fig. 13: UV-DRS Plot for (a) undoped and (b) doped nanocrystalline perovskites
Fig. 14: Effect of (a) and (a') Dye concentration; (b) and (b') Amount of catalyst; (c) and (c') pH on the photo catalytic degradation of the Victoria blue-B and Brilliant yellow dye for solar light irradiation (time 90 min)
Fig. 15: (a) Photo catalytic 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 nanocrystalline Perovskites.