CHAPTER - XI

SUMMARY AND CONCLUSIONS
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- In summary, nanostructures of Anatase and Rutile phases of TiO\textsubscript{2}, and higher weight percentages (4, 8, 12 & 16\%) of zinc (Zn), iron (Fe), manganese (Mn), cadmium (Cd) and strontium (Sr)-doped TiO\textsubscript{2} have been synthesized through sol-gel method. The prepared materials were characterized by various analytical tools such as XRD, FTIR, UV-V\textsubscript{i}s-DRS, PL, SEM with EDX and TGA/DTA. In addition, SHG/NLO efficiency and the photocatalytic activity of methylene blue (MB) dye degradation under sunlight using synthesized TiO\textsubscript{2} nanopowders were investigated.

- X-ray diffraction analysis (XRD) results predicted the phase, crystallite sizes and lattice parameters of the synthesized products. Hence, it confirms that the all samples attributed to the tetragonal structure. The rutile phase has increased crystallite size than that of anatase phase due to the higher annealing (750°C) temperature. In Zn-TiO\textsubscript{2} and Sr-TiO\textsubscript{2}, it can be concluded that the crystallite sizes were increased with higher weight percentages of dopants. The Fe-TiO\textsubscript{2}, Mn-TiO\textsubscript{2} and Cd-TiO\textsubscript{2} have decreased crystallite sizes with higher weight percentages of doping metal elements. Moreover, the crystallite sizes, lattice constants (‘a’ and ‘c’) and cell volumes (V) of metals doped TiO\textsubscript{2} were always higher than that of pure TiO\textsubscript{2}.

- Fourier Transform Infrared Spectroscopy (FTIR) identified the characteristic vibrational frequencies of TiO\textsubscript{2} nanomaterials. The metal-oxygen (Ti-O) bond was found invariably in all compositions, this indicates that the structure of TiO\textsubscript{2} was not altered even after the addition of metal dopants. Hence, the crystallinity and phase purity were good in pure and metals doped TiO\textsubscript{2} nanoparticles when compared to
as-synthesized TiO$_2$. Further, all the samples on doping exhibit shifting of bands as a result of introduction of metal ions.

- The allowed direct (hv vs. (ahv)$^2$) and indirect (Kubelka–Munk plot) band gap energies and crystallite sizes (Brus model) of the products were determined by UV-Vis-Diffuse Reflectance Spectroscopy (DRS) analysis. Hence, the direct and indirect $E_g$ values were near agreement with the calculated band gap energy. Compared to pure TiO$_2$, shift of the reflectance spectra of metals-doped TiO$_2$ nanoparticles towards the higher energy regions was observed. Hence, the optical band gap energies (eV) of metals-doped TiO$_2$ were always higher than that of pure TiO$_2$ and in the order of,

$$
\text{Rutile} < \text{Anatase} < \text{Fe-TiO}_2 < \text{Mn-TiO}_2 < \text{Zn-TiO}_2 < \text{Cd-TiO}_2 < \text{Sr-TiO}_2
$$

(3.25) (3.58) (3.66) (3.74) (3.75) (3.76) (3.82)

- The Photoluminescence (PL) analysis shows the existence of emissions in both UV and visible regions. However, Fe, Mn and Sr doped TiO$_2$ nanocomposites exhibit new PL phenomena. On the other hand, Zn-TiO$_2$ and Cd-TiO$_2$ exhibit the same PL emission features as pure TiO$_2$ with higher intensities.

- Doped materials may show potential response for optical properties but the response usually depends on the nature of the dopant ions. The absorption and luminescence properties are suitably changing with various morphological growths of different sizes of metal elements doped-TiO$_2$ nanostructures comparable to pure TiO$_2$.

- The products were found to be transparent in the entire visible region with cut-off wavelengths ($\lambda_{cut}$) within the UV region confirming its suitability for device fabrications.

- From the band gap energy values, the optimum level of doping for metal ions was estimated [Zn (8%), Fe (8%), Mn (12%), Cd (12%) and Sr (8%)].
Scanning Electron Microscopy (SEM) images of metals-doped TiO₂ show the well-defined particle like morphology, having abundance of spherical shaped nanoparticles with weak agglomeration. However, pure TiO₂ shows the non-uniform distribution of agglomerated particles. Furthermore, the particle size distribution results were consistent with the XRD and DRS (Brus model) measurements. However, the rutile phase has larger particle size than that of anatase TiO₂ indicate the thermal annealing could make impact on grain growth.

The chemical composition of the titania nanocomposites was confirmed by energy dispersive X-ray spectroscopy (EDX). It represent the relative atomic and weight percentages of corresponding metal elements such as Ti, O and, Zn, Fe, Mn, Cd and Sr, respectively for pure and metals doped TiO₂ nanoparticles.

The thermal decomposition and phase transition of pure and metal-doped TiO₂ nanostructures were determined by TGA and DTA analysis. From that, we conclude that the thermal stabilities have been increased after the introduction of doping metal elements into TiO₂ crystal framework. The residual weights (%) in the order of,

\[
\begin{align*}
\text{TiO}_2 &< \text{Mn-TiO}_2 < \text{Cd-TiO}_2 < \text{Zn-TiO}_2 < \text{Sr-TiO}_2 < \text{Fe-TiO}_2 \\
(68.13) &< (71.64) < (75.72) < (77.95) < (82.11) < (83.76)
\end{align*}
\]

The existence of second harmonic generation (SHG) signals was observed using Nd: YAG laser with fundamental wavelength of 1064 nm, to ensure the Nonlinear (NLO) activity of the materials. It confirms that the SHG efficiencies of metals-doped TiO₂ were always higher than that of pure TiO₂ with respect to KDP crystal in the order of,

\[
\begin{align*}
\text{TiO}_2 &< \text{Fe-TiO}_2 < \text{Mn-TiO}_2 < \text{Zn-TiO}_2 < \text{Cd-TiO}_2 < \text{Sr-TiO}_2 \\
(0.22) &< (0.38) < (0.47) < (0.54) < (0.78) < (0.83)
\end{align*}
\]
The photocatalytic activity of methylene blue (MB) dye degradation using pure and metals (Zn, Fe, Mn, Cd & Sr) doped TiO$_2$ nanoparticles under sunlight irradiation was carried out. The results reveal the photocatalytic efficiency of metals doped TiO$_2$ is always higher than that of pure TiO$_2$ and prefers the order,

\[ \text{Zn - TiO}_2 > \text{Fe - TiO}_2 > \text{Sr - TiO}_2 > \text{Mn - TiO}_2 > \text{Cd - TiO}_2 > \text{Pure TiO}_2 \]

It is evident that the metal ions act as the photogenerated electron trappers. These interns to prevent electron/hole recombination and enhances the photodegradation of methylene blue dye.

Because of this unique optical property, TiO$_2$ nanomaterials play a vital role in a variety of optoelectronic, semiconductor and sensor applications.

**SUGGESTIONS FOR FUTURE WORK**

The author has planned to synthesis the nanocrystalline titanium di-oxide doped with rest of the alkaline and transition metals of higher weight percentages by sol-gel method. The structural, dielectric, optical, electrical, thermal and morphological properties of the prepared nanomaterials have to be elucidated. Moreover, the author has interested to perform the High Resolution-Transmission Electron Microscopy (HR-TEM), Dielectrics, X-ray Photoelectron Spectroscopy (XPS), FT-Raman and Atomic Force Microscopy (AFM) analyses for the TiO$_2$ nanomaterials. The author has also planned to investigate the photocatalytic activity of other azo dyes (such as Methyl Orange, Rhodamine Blue, Brilliant Green, Congo Red etc) using the synthesized TiO$_2$ nanoparticles with varying pH, catalyst dosage, dye concentration and temperature, this forms the embryo for future course of action.