CHAPTER 2
SYNTHESIS AND CHARACTERIZATION OF MIXED METAL OXIDES

Mixed metal oxides can play an appreciable role in many areas of chemistry and physics. The unique electronic and magnetic properties obtained when combining two metal oxides. However, the most common use for mixed metal oxides has been in the area of photocatalysis. Developments in the field of mixed metal oxide have produced many significant and interesting results in all areas investigated.

In this chapter Mixed metal oxides have been synthesized using mechanochemical method and studied in detail. This chapter is divided into three sections. Section A - covers synthesis and characterization of Metal Germanate (AGeO$_3$). Section B - deals with synthesis and characterization of Metal Selenite (BSeO$_3$). Section C - covers, synthesis and characterization of Metal Titanate (CTiO$_3$) as photocatalyst. The products obtained were characterized in detail by Fourier transform infrared (FT-IR) spectroscopy, UV-visible diffuse reflectance spectrophotometer (UV-DRS), X-ray diffraction analysis (XRD), Energy dispersive x-ray spectroscopy (EDS) coupled with scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Thermogravimetric analysis (TGA) and surface area determination (BET) and conductance measurements.
Section-A

Synthesis and Characterization of Metal Germanate

(AGeO\textsubscript{3}, A= Ca and Mg) as Photocatalyst

2.1A Introduction:

The topic of this chapter is the study of pervoskite system synthesis and their characterization. Many investigations have been conducted with a view to rationalizing the design of perovskites, that is, to control the relationship between catalytic activity and chemical composition of crystalline ceramics known as perovskite type mixed oxides. The arche type perovskite is a mineral having the composition ABO\textsubscript{3}. It was first described in the 1830s by the geologist Gustav Rose, who named it after the Russian mineralogist Count Lev Alekserich von Perovski\textsuperscript{137}. One of the conditions for obtaining the perovskite structure is that electroneutrality must be maintained. The cation in the A-site might be Mono-, di-, or trivalent, while that in the B-site might be tri-, tetra-, or pentavalent. The catalytic activity of such mixed oxide perovskites can be greatly improved by partial substitution of the cations in the A- and/or B-sites. Moreover, the B-site cations may be partially reduced to form finely dispersed metallic species supported on the A-site cation oxide, which makes these materials ideal catalyst precursors for a range of reactions involving metals as active sides\textsuperscript{138-141}.

Mineralization of organic water pollutants using interaction between ultraviolet radiation and semi-conductor catalysts has a strong potential as it has been widely demonstrated in the recent years\textsuperscript{142}. Visible light-responsive photocatalysts have received considerable attention because visible light occupies the main part of solar light. The development of the future generation of photocatalytic materials is important for the efficient use of solar light. The past two decades have witnessed intensive studies within light induced mineralization of hazardous organic pollutant with use of TiO\textsubscript{2} photocatalyst\textsuperscript{143}. The literature survey shows that lot of work is available on synthesis of homogeneous photocatalyst of the type TiO\textsubscript{2}, ZnO, ZrO\textsubscript{2} and SnO\textsubscript{2} but little attention is given on synthesis of AGeO\textsubscript{3} perovskite photocatalyst and their applications.

There is need to the search for effective photocatalyst that lead to the study of heterogeneous oxides for environmental cleaning purpose. The fact that using energy to
eliminate environmental condition to increase emission of CO₂ resulting more global warming. However, this shows the way us to a dilemma not to use energy to achieve anti-pollution goal. Under such circumstances, we have come to a conclusion that, there is need of new material that can gently harmonizes the contaminated environment to restore original condition by using natural energy which is a part of the environment and low cost energy is supplied to our home life. One solution to that problem is photocatalyst. In present study, the structural and microstructural characteristics are determined for purpose of creating an inexpensive and non toxic photocatalysts.

Germanium oxide (GeO₂) is an important semiconductor material that has attracted much interest owing to its unique optical property and silica analogue. Moreover, nanostructured GeO₂ possesses the superior physical and chemical properties compared with its bulk counterparts. Nowadays, it is being widely used in optoelectronic devices, vacuum technology, and catalysis. For example, GeO₂ nanowires were used in one-dimensional luminescence nanodevices by Sahnoun et al., and GeO₂ nanotubes and nanorods as an important optical fibre material have been used in thermal vacuum test successfully by Jiang et al. It is well known that GeO₂ forms in two stable crystalline structures at an ambient temperature, the α-quartz trigonal structure and the rutile tetragonal structure.

The present section reports the synthesis and characterization of some AGeO₃ structure (where A= Ca and Mg). Various characterization techniques have been applied, namely: Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction analysis (XRD), Energy dispersive X-ray spectroscopy (EDS) coupled with scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Thermogravimetric analysis (TGA) and surface area determination (BET).

2.2A Experimental:

Metastable nanostructure and ultra fine grained materials are produced by a large variety of methods. Besides the incipient crystallization of amorphous solids, mechanochemical alloying is nowadays one of the widely used preparation techniques to obtain nanocrystalline structures. Mechanochemical alloying techniques involve the synthesis of materials by high-energy milling in which elemental blends (or ore-alloyed
powders, oxides, nitrates etc) are milled to achieve alloys or composite materials\textsuperscript{148-150}. High energy mechanochemical method offers indeed supplementary degree of freedom in the choice of possible routes for synthesizing new materials and found further as an attractive method of synthesis in view of its potential for large scale production. The products obtained by this method may be amorphous alloys, metastable crystalline phase, nanocrystalline materials and quasi crystals\textsuperscript{151-153}.

In this method, 1:1 ratio of analytical grade metal oxide (CaO and MgO) and GeO\textsubscript{2} were subjected to stepwise calcinations by heating till terminal temperature. The increase in temperature of muffle furnace was programmed at the rate 10 °C/ min from one temperature to the subsequent temperature for 12 hours. After heating at 600 °C the material was cooled and grounded with a gap of 3 hours using mortar and pestle. Later on the ground material was further heated at 900 °C for another 12 hours. Finally polycrystalline powders of AGeO\textsubscript{3} obtained were used for further characterization. The reaction stoichiometry of metal oxide and GeO\textsubscript{2} is given in Table 2.1A along with product.

**Table 2.1A: Reaction stoichiometry between metal oxide and GeO\textsubscript{2}**

<table>
<thead>
<tr>
<th>AO (1 mole)</th>
<th>GeO\textsubscript{2} (1 mole)</th>
<th>AGeO\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>GeO\textsubscript{2}</td>
<td>CaGeO\textsubscript{3}</td>
</tr>
<tr>
<td>MgO</td>
<td>GeO\textsubscript{2}</td>
<td>MgGeO\textsubscript{3}</td>
</tr>
</tbody>
</table>

The vibrational frequency of the synthesized photocatalysts was studied by Fourier Transform Infrared Spectroscopy (FT-IR), Shimadzu -8400S, in the range of 400-4000 cm\(^{-1}\). The optical property of synthesized product was studied by using Perkin Elmer- \(\lambda\) -950, UV-visible spectrophotometer over the range 200-800 nm. The phase compositions and structure properties of the material was studied using X-ray diffractometer (XRD), Rikagu-DMAX-250 with Cu K\(\alpha\) radiation, having \(\lambda=1.5406\) Å. The surface morphology and chemical compositions of synthesized catalyst was analyzed using a scanning Electron Microscope-JED-2300LA coupled with an Energy Dispersive Spectrometer-JED-23000La. Transmission Electron Microscopic images were recorded on Philips, CM-200. The effect of temperature on stability of the photocatalysts was
evaluated by thermogravimetry on Shimadzu TG-DTA 60M analyzer. Further, electrical conductivity was measured as a function of temperature.

2.3A Results and Discussion:

2.3.1A IR spectroscopy:

The infrared spectra are depicted in Fig. 2.1A (a and b) confirm the formation of AGeO₃ nanocrystalline photocatalyst after mechanochemical milling of metal oxides and GeO₂. As can be seen, the spectra of the product obtained by mechanochemical synthesis for 12 hours exhibit the vibration frequency band below 700 cm⁻¹ and confirm the presence of A-O bonds. Further Fig. 2.1A (a and b) shows peaks between 750 cm⁻¹ to 1000 cm⁻¹ assigned to the stretching vibrations of Ge-O.

2.3.2A Photophysical properties:

The photo-absorption of the photocatalyst depends on the mobility of electron-hole pairs, which determines the probability of electron and holes to reach reaction sites on the surface of the photocatalyst. Figure 2.2A (a and b) represent the UV-visible diffused reflectance spectra of synthesized CaGeO₃ and MgGeO₃ nanocrystalline photocatalyst. All the photocatalyst studied shows that the absorption shifts towards UV-visible region. The diffused reflectance spectra of CaGeO₃ and MgGeO₃ shows corresponding adsorption edge cut off at 390 nm and 370 nm respectively. These wavelengths are used to evaluate the band gap energies by the equation.

\[ E_g = h\nu = hc/\lambda = hc\bar{\nu} \]

Where \( E_g = \) band gap energy, \( h = \) Planks constant, \( c = \) velocity of light, \( \lambda = \) wavelength.

The synthesized photocatalyst shows the band gap energy 3.28 eV for CaGeO₃ and 3.45 eV for MgGeO₃.

A careful inspection of Fig.2.2A (a and b) shows broad absorption peaks, these broad absorption peaks may be due to uneven shape and size of AGeO₃ type photocatalyst. The result obtained implies that the sample may possess excellent photocatalytic activity.
Fig.2.1A: FT-IR spectra of a) CaGeO$_3$ and b) MgGeO$_3$
Fig. 2.2A: UV-DRS spectra of a) CaGeO$_3$, and b) MgGeO$_3$. 
2.3.3A X-ray diffraction:

Figure 2.3A (a and b) shows the XRD patterns of mechanochemically synthesized nanocrystalline mixed metal oxides CaGeO$_3$ and MgGeO$_3$. The presences of strong and sharp diffraction peaks at 2θ are located at 24.7, 27.1, 28.1, 29.2 and 48.6 which corresponds to (201), (121), (210), (120) and (303) crystal planes for CaGeO$_3$ and for MgGeO$_3$. 2θ values are present at 27.5, 27.6, 29.6, 30.1, 35.3 and 38.8 corresponding to (420), (221), (321), (610), (521) and (711) crystal planes. The crystal planes indicates the formation of triclinic and orthorhombic AGeO$_3$ with the space group [P1(2) and P bca] and d-line pattern matches well with reported JCPDS data card no.21-0142 for CaGeO$_3$ and 34-0281 for MgGeO$_3$.

The average particle sizes were calculated using Debye-Scherrer formula.

$$D_{(hkl)} = \frac{k \lambda}{\beta \cos \theta}$$

The average crystalline size of CaGeO$_3$ is 83 nm and 68 nm for MgGeO$_3$. The observed particle size may be due to specific surface area.

2.3.4A SEM analysis:

Figure 2.4A (a and b) shows the SEM morphology of the synthesized nanocrystalline metal germanate (AGeO$_3$) powders prepared at 1000 °C for 12 hours using mechanochemical method. The powders obtained contain a large portion of agglomerates with a small particulate size and some of shows multilayer deposition. Since the agglomeration was sufficiently large and soft. It could be clearly observed that the agglomerates are actually formed very small particles in nanometric range size. Although the agglomerates are of irregular size the fine nanometric particles are mostly below 100 nm in size. MgGeO$_3$ particles are found to be bigger with cubic shape.

The EDS analysis was employed to determine the composition of pure AGeO$_3$ nanocrystalline photocatalyst. The results obtained matches well with the reaction stoichiometry.
Fig. 2.3A: XRD pattern of a) CaGeO$_3$, and b) MgGeO$_3$
**Fig. 2.4A:** SEM images of a) CaGeO$_3$, and b) MgGeO$_3$
Fig. 2.5A: TEM and SAED images of a) CaGeO$_3$, and b) MgGeO$_3$. 
2.3.5A TEM analysis:

The TEM images along with the selected area of electron diffraction pattern (SAED) recorded corresponding to CaGeO$_3$ and MgGeO$_3$ are shown in Fig.2.5A (a and b). The TEM’s reveals that, the nanoparticles are elliptical and linked to each other. The dark spot in the TEM micrograph can be alluded to CaGeO$_3$ (Fig.2.5 A (a)) and MgGeO$_3$ (Fig.2.5A (b)) nanoparticles as SAED pattern associated with such spots reveals occurrence of triclinic and orthorhombic structures and are in good agreement with the XRD data. The average size of the CaGeO$_3$ and MgGeO$_3$ nanocrystals was found in the range of 70 to 80 nm.

2.3.6A BET Surface area analysis:

The N$_2$ adsorption isotherms of synthesized CaGeO$_3$ and MgGeO$_3$ are shown in Fig.2.6A (a and b). It reveals that all the synthesized metal selenite photocatalyst have typical IV N$_2$ adsorption-desorption isotherms with H$_1$ hysteresis which indicates that the samples preserve the cylindrical mesopores. The BJH pore size distribution demonstrates that all the samples have a narrow pore diameter range. Pore volume (single point total pore volume of pores at P/P$_o$), pore size (determined from BJH desorption isotherm) and BET specific surface area of the samples are given in Table 2.2A.

Results obtained for BET shows that the surface area is more for MgGeO$_3$ and is 30.950 m$^2$/gm and 3.117 m$^2$/gm for CaGeO$_3$. Pore volume is 0.034 and 0.121 for CaGeO$_3$ and MgGeO$_3$ respectively.

2.3.7A TG-DTA analysis:

The TG curve in Fig.2.7A shows no weight loss observed upto 900 °C. The clear plateau formed on TG curve indicates the stability of the product formed.

On the DTA curve a main endothermic effect was observed at 390 to 450 °C with a minimum at about 420 °C for CaGeO$_3$ (Fig 2.7A (a)) and for MgGeO$_3$ (Fig 2.7A (b)) endothermic effect was observed at 500 to 700 °C with a minimum at about 600 °C. No further weight loss and no thermal effect observed in both indicating the stability of the product formed.
Fig. 2.6A: N$_2$ adsorption-desorption isotherms of synthesized a) CaGeO$_3$, and b) MgGeO$_3$
Fig. 2.7A: TG-DTA of a) CaGeO$_3$, and b) MgGeO$_3$
### Table 2.2A: N₂ adsorption-desorption results for the metal germanate photocatalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET area (m²/gm)</th>
<th>Pore volume (cc/g)</th>
<th>Pore size(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaGeO₃</td>
<td>3.117</td>
<td>0.034</td>
<td>438.6</td>
</tr>
<tr>
<td>MgGeO₃</td>
<td>30.95</td>
<td>0.121</td>
<td>157.2</td>
</tr>
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### Table 2.3A: Activation energy for metal germanate photocatalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pauling scale for AGeO₃</th>
<th>Energy of activation KJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaGeO₃</td>
<td>1.00</td>
<td>0.52</td>
</tr>
<tr>
<td>MgGeO₃</td>
<td>1.31</td>
<td>0.63</td>
</tr>
</tbody>
</table>
2.3.8A Electrical properties:

The thin films were prepared for the I-V characteristic and electrical conductivity studies. Ethyl cellulose used as solid binder for making of films. First ethyl cellulose is added in mortar and few drop of organic binder (Organic binder contains organic solvent and is evaporated at 500 °C) was added after 20 min, then add sample (ethyl cellulose: sample ratio is 1:10) and make a paste. This material is used for making films by using the screen printing. These films were heated at 550 °C for 1 hour to evaporate the organic binder. These films were used for the determination of I-V characteristic and electrical conductivity.

Fig. 2.8A (a) shows the I-V characteristic of films of CaGeO₃ and MgSeO₃ at room temperature. Here voltage was continuously varied with constant room temperature and change in conductance was recorded. I-V characteristics are observed to be symmetrical in nature, indicating the ohmic nature of nanocrystalline materials.

Electrical conductivities for synthesized nano AGeO₃ are shown in Fig. 2.8A (b). Electrical performance of the material was studied by measuring change in conductance with temperature. The dependence of conductivity of metal germanate films in air ambience. The conductivity of the film goes on increasing with increase in temperature, indicating negative temperature coefficient (NTC) of resistance. This shows the semiconducting nature of the materials.

Fig. 2.8A (b) depicts the variation of electrical conductivity as a function of temperature. Activation energies were estimated from the slope of log $\sigma$ versus 1/T curve. Activation energies obtained for CaGeO₃ and MgGeO₃ are found to be 0.52 kJ / mole and 0.63 kJ / mole respectively (Table 2.3A). The observed trend is explained on the basis of ionic size of Ca and Mg. The trend in observed activation energy is in the reverse order of ionic radii. Smaller ion carries more current and hence shows decrease in activation energy.
Fig. 2.8A: a) IV Characteristic of AGeO$_3$, and b) electrical conductivity of AGeO$_3$.
Section-B

Synthesis and Characterization of Metal Selenite
(BSeO₃, B= Zn, Pb, Mg and Cu) as Photocatalyst

2.1B Introduction:

Metal oxides generally suffer from a drawback of low surface area. In order to overcome this, they are either combined with other metal oxides or supported with some catalytically inactive materials. These mixed metal oxides can be prepared by various methodologies like wet impregnation, co-precipitation, sol-gel and combustion techniques. Usually, the precursors employed are their metal salts or organo metallic species. These precursors are diluted and further hydrolysed to obtain their corresponding hydroxides. The hydroxides are then dried and calcined to obtain the desired mixed metal oxides. The mole ratio of the precursors used is directly proportional to mole ratio of metal oxides in the prepared mixed metal oxides. Thus, mixed metal oxides can be fine tuned to obtain the desired catalytic activity.

In this work, we have studied the properties of some BSeO₃ structure (where B= Zn, Pb, Mg and Cu). Various characterization techniques have been applied, namely: Fourier transform infrared (FT-IR) spectroscopy, UV-visible diffuse reflectance system spectrophotometer (UV-DRS), X-ray diffraction analysis (XRD), Energy dispersive X-ray spectroscopy (EDS) coupled with scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and surface area determination (BET).

2.2B Experimental:

Analytical grade metal oxide (ZnO, PbO, MgO and CuO) and SeO₂ with equimolar ratio were subjected to stepwise calcinations by heating till terminal temperature. The increase in temperature of muffle furnace was programmed at the rate 10 °C/ min from one temperature to the subsequent temperature for 12 hours. After heating at 200 °C the material was cooled and grounded with a gap of 3 hours using mortar and pestle. Later on the ground material was further heated at 320 °C for another 12 hours. Finally, polycrystalline powders of BSeO₃ obtained were used for further
characterization. The reaction stoichiometry of metal oxides and SeO$_2$ for the synthesis of mixed metal oxide is given in Table 2.1B along with product.

**Table 2.1B:** Reaction stoichiometry between metal oxides and SeO$_2$

<table>
<thead>
<tr>
<th>BO (1 mole)</th>
<th>SeO$_2$ (1 mole)</th>
<th>BSeO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>SeO$_2$</td>
<td>ZnSeO$_3$</td>
</tr>
<tr>
<td>PbO</td>
<td>SeO$_2$</td>
<td>PbSeO$_3$</td>
</tr>
<tr>
<td>MgO</td>
<td>SeO$_2$</td>
<td>MgSeO$_3$</td>
</tr>
<tr>
<td>CuO</td>
<td>SeO$_2$</td>
<td>CuSeO$_3$</td>
</tr>
</tbody>
</table>

The vibrational frequency of the synthesized photocatalysts was studied by Fourier Transform Infrared Spectroscopy (FT-IR), Shimadzu -8400S, in the range of 400-4000 cm$^{-1}$. The optical property of synthesized products was studied by using Perkin Elmer- $\lambda$ -950, UV-visible spectrophotometer over the range 200-800 nm. The phase compositions and structure properties of the material was studied using X-ray diffractometer (XRD), Rikagu-DMAX-250 with CuK$\alpha$ radiation, having $\lambda$ = 1.5406 Å. The surface morphology and chemical compositions of synthesized catalyst was analyzed using a Scanning Electron Microscope-JED-2300LA coupled with an Energy Dispersive Spectrometer-JED-23000La. Transmission Electron Microscopic images were recorded on Philips, CM-200.

**2.3B Results and Discussion:**

**2.3.1B IR spectroscopy:**

IR spectra of all the products were taken in the region of 400-1250 cm$^{-1}$ using KBr pellets on a computer interfaced shimadzu FT-IR spectrophotometer. The infrared spectra depicted in Fig 2.1B (a-d) confirm the formation of BSeO$_3$ nanocrystalline photocatalyst after mechanochemical milling of metal oxides and SeO$_2$. The pervoskite obtained by mechanochemical synthesis after 12 hours exhibit the vibration frequency band below 500 cm$^{-1}$ and confirm the presence of B-O bonds. Figure 2.1B (a-d) also reveals that peaks between 850 cm$^{-1}$ to 650 cm$^{-1}$ assigned to the stretching vibrations of Se-O.
Fig. 2.1B: FT-IR spectra of a) ZnSeO$_3$, b) PbSeO$_3$, c) MgSeO$_3$, and d) CuSeO$_3$
2.3.2B Photophysical properties:

Figure 2.2B (a-d) represent the UV-visible diffused reflectance spectra of mechanochemically synthesized ZnSeO₃, PbSeO₃, MgSeO₃ and CuSeO₃ nanocrystalline pervoskite photocatalyst. All the photocatalyst studied shows that the absorption shifts towards UV-visible region. The diffused reflectance spectra of ZnSeO₃, PbSeO₃, MgSeO₃ and CuSeO₃ shows corresponding absorption edge cut-off at 354 nm, 337 nm, 370 nm, 406 nm respectively. The band gaps of the photocatalysts are estimated to be 2.8 to 3.4 eV from the onset of the absorption edge (Table 2.2B).

Figure 2.2B (a-d) depicts broad absorption peaks, these broad absorption peaks may be due to uneven shape and size of BSeO₃ type photocatalyst. The results obtained imply that the sample may possess excellent photocatalytic activity.

2.3.3B X-ray diffraction:

The X-ray diffraction patterns of mechanochemically synthesized nanocrystalline mixed metal oxides ZnSeO₃, PbSeO₃, MgSeO₃ and CuSeO₃ are represented in Fig.2.3B. The presence of strong and sharp diffraction peaks at 2θ are located at 25.9, 29.9, 32.8, 33.0, 38.3, 39.5 and 42.4 corresponding to (111), (200), (210), (121), (220), (031) and (231) crystal planes for ZnSeO₃, for PbSeO₃ 2θ values are present at 26.1, 26.82, 32.5 corresponding to (100) crystal planes, for MgSeO₃ 2θ values are present at 26.1, 30.4, 32.8, 33.1 corresponding to (111), (200), (210), (121) crystal planes and for CuSeO₃ 2θ values are located at 29.7,31.3,33.4,35.5,38.9 corresponding to (200), (210), (121), (211), (220) crystal planes. The crystal planes indicates the formation of orthorhombic BSeO₃ with the space group (Pmmm) and d-line pattern matches well with reported JCPDS data card no.31-1473, 21-0479, 31-0806 and 20-0686, 31-0479 respectively.

The average particle sizes were calculated using Debye-Scherrer formula and calculated results shown in Table 2.3B.

Table 2.3B shows that the average crystalline size is larger for MgSeO₃ and smaller for ZnSeO₃. It may be due to specific surface area of mixed metal oxide.
Fig. 2.2B: UV-DRS spectra of a) ZnSeO₃, b) PbSeO₃, c) MgSeO₃, and d) CuSeO₃
### Table 2.2B: Band gap energy for different metal selenites

<table>
<thead>
<tr>
<th>Metal selenite</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSeO$_3$</td>
<td>3.228</td>
</tr>
<tr>
<td>PbSeO$_3$</td>
<td>3.390</td>
</tr>
<tr>
<td>MgSeO$_3$</td>
<td>3.088</td>
</tr>
<tr>
<td>CuSeO$_3$</td>
<td>2.811</td>
</tr>
</tbody>
</table>

### Table 2.3B: Crystalline size of different metal selenites

<table>
<thead>
<tr>
<th>Metal selenite</th>
<th>Crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSeO$_3$</td>
<td>20</td>
</tr>
<tr>
<td>PbSeO$_3$</td>
<td>43</td>
</tr>
<tr>
<td>MgSeO$_3$</td>
<td>57</td>
</tr>
<tr>
<td>CuSeO$_3$</td>
<td>38</td>
</tr>
</tbody>
</table>
Fig. 2.3B: XRD pattern of a) ZnSeO$_3$, b) PbSeO$_3$, c) MgSeO$_3$, and d) CuSeO$_3$
2.3.4B SEM analysis:

The crystal morphology of as prepared BSeO₃ powder was investigated by scanning electron microscopy (SEM). The SEM photograph shows that the size of the catalyst ranging from 50 to 100 nm. All synthesized BSeO₃ type photocatalyst shows uniform particle size.

All SEM micrograph shows that, crystals have irregular shape and most of the smaller crystals are agglomerated. The agglomerates can be “soft” if they consist of a number of particles held together by weak Van der Waals forces or “hard” if the particles inside the agglomerates are held together by stronger chemical or sintering bonds. In our study there was no noticeable difference in morphologies of investigated powders (Fig.2.4B (a-d)). Some other explanations for differences in densification behaviour of the investigated samples should be considered.

The EDS analysis was employed to determine the composition of pure BSeO₃ nanocrystalline photocatalyst. The results obtained matches well with the reaction stoichiometry.

2.3.5B TEM analysis:

Figure 2.5B (a-d) shows typical TEM and SAED images of the BSeO₃ nanocrystalline materials. Average sizes of the BSeO₃ estimated from TEM images are in the range of 20 to 100 nm. The observed aggregation of the BSeO₃ nanocrystals may be due to the high surface energy of the photocatalyst. The SAED pattern associated with dark spots in all pictures confirms orthorhombic BSeO₃ is in total agreement with the XRD data.
Fig. 2.4B: SEM images of a) ZnSeO$_3$, b) PbSeO$_3$, c) MgSeO$_3$, and d) CuSeO$_3$
Fig. 2.5B: TEM and SAED images of a) ZnSeO$_3$, b) PbSeO$_3$, c) MgSeO$_3$, and d) CuSeO$_3$
2.3.6B BET surface area analysis:

Figure 2.6B (a-c) shows N\textsubscript{2} adsorption isotherms of synthesized ZnSeO\textsubscript{3}, MgSeO\textsubscript{3} and CuSeO\textsubscript{3}. It reveals that all the synthesized metal selenite photocatalyst have typical N\textsubscript{2} adsorption-desorption isotherms with H\textsubscript{1} hysteresis which indicates that the samples preserve the cylindrical mesopores. The BJH pore size distribution demonstrates that all the samples have a narrow pore diameter range. Pore volume (single point total pore volume of pores at P/P\textsubscript{o}), Pore size (determined from BJH desorption isotherm) and BET specific surface area of the samples are given in Table 2.4B.

2.3.7B Electrical properties:

The thin films were prepared for the measurements of I-V characteristic and electrical conductivity studies. Ethyl cellulose was used as solid binder for making of films. First ethyl cellulose is added in mortar and then few drop of organic binder (Organic binder contains organic solvent which is evaporated at 500 °C) after 20 min, add sample (ethyl cellulose: sample ratio is 1:10) and make a paste. This is used for making films by using the screen printing. These films were heated at 550 °C for 1 hour to evaporate the organic binder. These films were used for the determination of I-V characteristics and electrical conductivity.

Figure 2.7B (a) shows the I-V characteristics of films of ZnSeO\textsubscript{3}, PbSeO\textsubscript{3}, MgSeO\textsubscript{3} and CuSeO\textsubscript{3} at room temperature. Here voltage was continuously varied with constant room temperature and change in conductance was recorded. I-V characteristic are observed to be symmetrical in nature, indicating the ohmic nature of nanocrystalline materials.

Electrical conductivities for synthesized nano BSeO\textsubscript{3} are shown in Fig.2.7B (b). Electrical performance of the material was studied by measuring change in conductance with temperature. The dependence of conductivity of metal selenite films in air ambience. The conductivity of the film goes on increasing with increase in temperature, indicating negative temperature coefficient (NTC) of resistance. This shows the semiconducting nature of the materials.
Fig. 2.6B: N₂ adsorption-desorption isotherms of synthesized a) ZnSeO₃, b) MgSeO₃, and c) CuSeO₃.
### Table 2.4B: N₂ adsorption-desorption results for the metal selenites photocatalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET area (m²/gm)</th>
<th>Pore volume (cc/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSeO₃</td>
<td>7.648</td>
<td>0.0091</td>
<td>47.68</td>
</tr>
<tr>
<td>MgSeO₃</td>
<td>6.83</td>
<td>0.00174</td>
<td>101.9</td>
</tr>
<tr>
<td>CuSeO₃</td>
<td>3.579</td>
<td>0.00599</td>
<td>67.02</td>
</tr>
</tbody>
</table>

### Table 2.5B: Activation energy for metal selenite photocatalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pauling scale for BSeO₃</th>
<th>Energy of activation KJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSeO₃</td>
<td>1.31</td>
<td>1.95</td>
</tr>
<tr>
<td>ZnSeO₃</td>
<td>1.65</td>
<td>2.01</td>
</tr>
<tr>
<td>CuSeO₃</td>
<td>1.95</td>
<td>2.18</td>
</tr>
<tr>
<td>PbSeO₃</td>
<td>2.33</td>
<td>4.15</td>
</tr>
</tbody>
</table>
Fig. 2.7B (b) depicts the variation of electrical conductivity as a function of temperature. Activation energies were estimated from the slope of log $\sigma$ versus $1/T$ curve. Activation energies obtained for MgSeO$_3$, ZnSeO$_3$, CuSeO$_3$ and PbSeO$_3$ are found to be 1.95, 2.01, 2.18 and 4.15 kJ / mole respectively (Table 2.5B). The observed trend is explained on the basis of ionic size of Mg, Zn, Cu and Pb. The observed trend in activation energies are in reverse order of ionic radii. Smaller ion carries more current and hence shows decrease in activation energy.
Fig. 2.7B: a) I-V Characteristic of BSeO$_3$, and b) electrical conductivity of BSeO$_3$. 

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Synthesis and Characterization of Metal Titanate
\((\text{CTiO}_3, \text{C} = \text{Ca, Pb, and Zn})\) as photocatalyst

2.1C Introduction:

In recent years, with the development of the industry, the dyes and pigments have been employed in a considerable way. The chromophores of the ionic and non-ionic dyes, which have complex chemical structure and are difficult to be degraded biologically under aerobic condition, are usually anthraquinone type or azo groups. Although the azo dyes such as methyl violet may not be directly toxic, they could come into being the carcinogenic compounds, e.g., aromatic amines degraded from the azo dyes under anaerobic condition. Solar energy, an abundant natural energy source, can be widely utilized in the photocatalytic degradation of the dyes and pigments. Recently, the role of photocatalytic oxides, which can be applied for colour removal and organic degradation of pollutants, is more and more important since they have some advantages over other materials, e.g., their low price, simple preparation, high photochemical stability and safety to the environment. The solar catalytic activity of oxides has attracted widespread attention to several reasons such as limitless solar light energy and recycled photocatalytic oxides. The past two decades have witnessed intensive studies within light induced mineralization of hazardous pollutant with use of TiO\(_2\)\(^{154-161}\) and ZnO\(^{158-164}\) photocatalyst and attracted extensive interest to solve the environmental and energy problem\(^{165}\). Many researchers work on these metal oxides semiconductors photocatalysis and have become more appealing than conventional oxidation methods. Semiconductor photocatalysis has been intensively studied in recent decades for a wide variety of application such as hydrogen production from water splitting and water and air treatment. Semiconductors are inexpensive, non-toxic and capable of extended use without substantial loss of photocatalytic activity. The majority of photocatalysts are, however, wide band-gap semiconductors which are active only under UV irradiation. In order to effectively utilize visible solar radiation, here is need to investigate various type of visible-light active photocatalysts including metal ion-doped TiO\(_2\), mixed metal oxides,
nanocomposites. It may be easily recovered by filtration and centrifugation. But little attention is given on photocatalyst\textsuperscript{166,167} of the type ABO\textsubscript{3} mixed metal oxides.

Metal titanate belongs to the important group of compounds with a perovskite. Calcium Titanate is well known for its high dielectric, luminescent and semiconductor properties\textsuperscript{168,169}. It is also used as photocatalysis on decomposition of water under UV light irradiation\textsuperscript{170}. In literature survey, calcium titanate has been prepared by combustion\textsuperscript{171}, organic–inorganic solution\textsuperscript{172}, sol–gel\textsuperscript{173}, polymeric precursor\textsuperscript{174}, co-precipitation and hydrothermal method\textsuperscript{175}. PbTiO\textsubscript{3} is well known for it’s widely used in optoelectrics, sensors, transducers and non volatile memory devices due to its remarkable ferroelectric, pyroelectric and pizoelectrical properties\textsuperscript{176}. In literature survey, lead titanate has been prepared by combustion\textsuperscript{177}, sol–gel\textsuperscript{178}, polymeric precursor\textsuperscript{179}, co-precipitation\textsuperscript{180} and hydrothermal method\textsuperscript{181}. ZnTiO\textsubscript{3} with perovskite structure is a potential candidate for applications in microwave dielectrics, gas sensors, absorbents for the desulfurization of hot coal gases and paint pigments\textsuperscript{182-188}. Zinc titanate has been prepared by sol–gel\textsuperscript{189,190}, co-precipitation and hydrothermal method.

Many of these methods are not cost effective and not ecofriendly. Therefore, it is still desirable to develop an alternative method for ecofriendly synthesis of CTiO\textsubscript{3} type of photocatalyst.

\textbf{2.2C Experimental:}

In the present study metal titanates were prepared using mechanochemical method. For the synthesis of CTiO\textsubscript{3} the molar ratio of CO and TiO\textsubscript{2} metal oxide was taken. (Where C= Zn, Pb and Ca).

\begin{table}
\centering
\caption{Reaction stoichiometry between metal oxide and TiO\textsubscript{2}}
\begin{tabular}{|c|c|c|}
\hline
\textbf{CO (1 mole)} & \textbf{TiO\textsubscript{2} (1 mole)} & \textbf{CTiO\textsubscript{3}} \\
\hline
PbO & TiO\textsubscript{2} & PbTiO\textsubscript{3} \\
\hline
CaO & TiO\textsubscript{2} & CaTiO\textsubscript{3} \\
\hline
ZnO & TiO\textsubscript{2} & ZnTiO\textsubscript{3} \\
\hline
\end{tabular}
\end{table}
The mixture was subjected to stepwise calcinations by heating till terminal temperature in muffle furnace at the rate 10 °C/min from one temperature to the subsequent temperature for 12 hours. After heating at higher temperature the material was cooled and grinded with a gap of 2 hours by using mortar and pestle. Later on, the grinded material was further heated at 900 °C for 12 hours for PbTiO₃. For ZnTiO₃ and CaTiO₃ the grinded material was further heated at 1000 °C for 20 hours. Finally, powder of CaTiO₃ obtained was used for further characterization.

Fourier Transform Infrared Spectroscopy (FT-IR), Shimadzu -8400S, in the range of 400-4000 cm⁻¹ was employed to see different modes of vibrations. Perkin Elmer- λ -950, UV-visible diffused reflectance spectrophotometer over range 200-800 nm was used to check optical properties. The phase compositions and structure properties of the material was studied using X-ray diffractometer (XRD), Rikagu-DMAX-250 with CuKα radiation, having λ= 1.5406 Å. Scanning Electron Microscope-JED-2300LA coupled with an Energy Dispersive Spectrometer-JED-23000La was used to check the surface morphology. The effect of temperature on stability of the photocatalysts was evaluated by thermogravimetry on Shimadzu TG-DTA-60M analyser.

2.3 Results and Discussion:
2.3.1 FT-IR analysis:
Figure 2.1 (a) represent FT-IR spectrum of CaTiO₃. A band around 688.54 cm⁻¹, 655.75 cm⁻¹, 613.32 cm⁻¹, 459.03 cm⁻¹, 412.74 cm⁻¹ and 374.16 cm⁻¹ are possibly caused by the stretching vibration due to the interactions produced between the oxygen and the metal bonds. Similarly for the PbTiO₃ in Fig.2.1 (b) shows a band around 439.00 cm⁻¹, 536.00 cm⁻¹, 653.00 cm⁻¹ and 757.00 cm⁻¹. ZnTiO₃ is represented in Fig.2.1 (c). A band around 372.00 cm⁻¹, 478.00 cm⁻¹, 574.00 cm⁻¹, 686.00 cm⁻¹, 713.00 cm⁻¹ and 740.00 cm⁻¹ is observed for ZnTiO₃ (Fig.2.1 (c)).

The O-O vibration of the peroxo group was within the range of 900.00 cm⁻¹ to 1000.00 cm⁻¹. The bands appear at 1200 cm⁻¹ to 1500 cm⁻¹ are due to the unantisymmetric and symmetric stretching vibrational modes of metal-oxygen bond. There was no peak found in the region of 3400 cm⁻¹ and it clearly shows that absence of moisture and water molecule.
Fig. 2.1C: FT-IR spectra of a) CaTiO₃, b) PbTiO₃, and c) ZnTiO₃
2.3.2C UV-DRS analysis:

The photo-absorption of the photocatalyst depends on the mobility of electron-hole pairs, which determines the probability of electron and holes to reach reaction sites on the surface of the photocatalyst. Figure 2.2C (a-c) represent the UV-visible diffused reflectance spectra of mechanochemically synthesized CaTiO$_3$, PbTiO$_3$ and ZnTiO$_3$ nanocrystalline photocatalyst. All the photocatalyst studied shows that the absorption shifts towards UV-visible region. The diffused reflectance spectra of CaTiO$_3$, PbTiO$_3$ and ZnTiO$_3$, shows corresponding absorption edge cut-off at 355 nm, 382 nm and 365 nm respectively. These wavelengths are used to evaluate the band gap energies. The synthesized photocatalyst shows the band gap in the range of 3.2 to 3.7 eV and are listed in Table 2.2C.

A careful inspection of Fig 2.2C (a-c) shows broad absorption peaks, these broad absorption peaks may be due to uneven shape and size of CTiO$_3$ type photocatalyst. The result obtained implies that the sample may possess excellent photocatalytic activity.

2.3.3C X-ray diffraction:

Figure 2.3C (a-c) represents the XRD patterns of mechanochemically synthesized nanocrystalline mixed metal oxides CaTiO$_3$, PbTiO$_3$, and ZnTiO$_3$.

The polycrystalline nature of calcium titanate powder is expressed by XRD pattern as shown in Fig.2.3C (a), which was identified as an orthorhombic phase. The presence of diffraction peaks can be used to evaluate the structural order at long range or periodicity of the material. Observed X-ray diffraction pattern for CaTiO$_3$ nanoparticles shows high degree of crystallinity. All the peaks in XRD pattern match well with reported characteristic reflection peaks of CaTiO$_3$ (JCPDS Card No.22-0153). The value of 2θ at 23.2, 32.8, 33.1, 47.5, 59.3 and 69.4 correspond to the plane (101), (200), (121), (040), (042), and (242). The CaTiO$_3$ shows the orthorhombic geometry with space group Pnma (62) and the crystallite size have been estimated and found to be 90 nm for CaTiO$_3$.

The XRD pattern of as prepared PbTiO$_3$ nanoparticle is represented in Fig.2.3C (b). The presence of diffraction peaks can be used to evaluate the structural order at long range or periodicity of the material.
Fig. 2.2C: UV-DRS pattern of a) CaTiO$_3$, b) PbTiO$_3$, and c) ZnTiO$_3$
Fig. 2.3C: XRD pattern of a) CaTiO$_3$, b) PbTiO$_3$, and c) ZnTiO$_3$
Table 2.2C: Band gap energies for metal titanate

<table>
<thead>
<tr>
<th>Metal titanate</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTiO₃</td>
<td>3.35</td>
</tr>
<tr>
<td>CaTiO₃</td>
<td>3.6</td>
</tr>
<tr>
<td>ZnTiO₃</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table 2.3C: Crystalline size of different metal titanate

<table>
<thead>
<tr>
<th>Metal titanate</th>
<th>Crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaTiO₃</td>
<td>90</td>
</tr>
<tr>
<td>PbTiO₃</td>
<td>64</td>
</tr>
<tr>
<td>ZnTiO₃</td>
<td>127</td>
</tr>
</tbody>
</table>
The importance features of the XRD data pertaining to obtained patterns with reference to finger printing with reported data for tetragonal phase of PbTiO₃ (JCPDS card no. 06-0452) and no other impurity phases were detected. It is found that all diffraction peaks of PbTiO₃ nanoparticle can be assigned to the tetragonal pervoskite. The value of 2θ at 22.7, 31.4, 32.4, 39.1, 46.5, 57.2 and 65.6 correspond to the plane (100), (101), (110), (111), (200), (211), and (202). The average grain size of sample estimated and found to be 64 nm for PbTiO₃. The XRD pattern of mechanochemical synthesized ZnTiO₃ represented in Fig 2.3C (c). ZnTiO₃ phase was confirmed by the comparison with standard JCPDS data card No. 26-1500. The value of 2θ at 23.9, 32.7, 35.3, 40.4 and 48.9 correspond to the plane (012), (104), (110), (113), and (024). The average particle size was calculated using Scherrer formula and found to be 127 nm. The ZnTiO₃ shows the rhombohedral geometry with space group R 3(148).

The average particle sizes were calculated using Debye-Scherrer formula and results obtained are shown in Table 2.3 C.

2.3.4C SEM analysis:

Figure 2.4C (a-c) represents scanning electron of the synthesized nanocrystalline metal titanate (CTiO₃) powders prepared at 1000 °C for 12 hours using mechanochemical method. The powders obtained contain a large portion of agglomerates with a small particulate size. Since the agglomeration was sufficiently small and soft. It could be clearly observed that the agglomerates are actually formed very small particles in nanometric range size.

Effect of dwell time on the morphology of the calcined powders was found to be quite significant. It is clearly seen that longer heat treatment led to larger particles and hard agglomeration. The particle size found to be below 100 nm for CTiO₃ samples and the agglomerates are of irregular in shape. The SEM image shows nanoparticles with good uniformity and crystallinity.
Fig. 2.4C: SEM images of a) CaTiO₃, b) PbTiO₃, and c) ZnTiO₃
Fig 2.4C (b) shows significant amount of porosity which corroborate the low sintered density of the sample. The porosity present in the samples are intergranular in nature, the intragranular pores are not observed. Form the microstructure it is very difficult to identify the grain size. It seems that small grains are fused and formed large mass. These agglomerates can be soft if they consist of a number of particles held together by weak van der waals forces or hard if the particles inside the agglomerates are held together by strong chemical or sintering bonds.

2.3.5C BET Surface area analysis:

Table 2.4C revels surface area obtained for mechanochemically synthesized CaTiO₃, PbTiO₃ and ZnTiO₃ using N₂ adsorption desorption isotherm. It shows that all the synthesized metal titanate photocatalyst have typical N₂ adsorption-desorption isotherms with H₁ hysteresis which indicates that the samples preserve the cylindrical mesopores. The BJH pore size distribution demonstrates that all the samples have a narrow pore diameter range. Pore volume (Single point total pore volume of pores at P/Pₒ), pore size (determined from BJH desorption isotherm) and BET specific surface area of the samples.

2.3.6C TG-DTA:

The thermal analysis curve (Fig.2.5C (a-c)) shows no significant weight loss is seen for CTiO₃ nanocrystalline product and thermally stable upto 1000 °C.

Differential thermal analysis also clearly indicates the extreme stability as well as no abrupt change, gives no evidence for further reaction (Fig. 2.5 C).
Fig. 2.5C: TG-DTA of a) CaTiO₃, b) PbTiO₃, and c) ZnTiO₃
Table 2.4C: N2 adsorption-desorption results for the metal titanate photocatalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET area (m²/gm)</th>
<th>Pore volume (cc/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaTiO₃</td>
<td>301.1</td>
<td>0.02467</td>
<td>210.0</td>
</tr>
<tr>
<td>PbTiO₃</td>
<td>282.2</td>
<td>0.02354</td>
<td>250.6</td>
</tr>
<tr>
<td>ZnTiO₃</td>
<td>330.2</td>
<td>0.03102</td>
<td>423.5</td>
</tr>
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</table>

Table 2.5C: Activation energy for metal titanate photocatalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pauling scale</th>
<th>Energy of activation KJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaTiO₃</td>
<td>1.00</td>
<td>0.757</td>
</tr>
<tr>
<td>ZnTiO₃</td>
<td>1.65</td>
<td>0.946</td>
</tr>
<tr>
<td>PbTiO₃</td>
<td>2.33</td>
<td>1.176</td>
</tr>
</tbody>
</table>
2.3.7C Electrical properties:

The thixotropic paste was obtained by mixing ethyl cellulose use as solid binder for making of films. First ethyl cellulose in mortar and add few drop of organic binder (Organic binder which contains organic solvent which is evaporated at 500 °C) wait for 20 min, then add sample (ethyl cellulose: Sample ratio is 1:10) and make a paste. This is used for making films by using the screen printing. These films were heated at 550 °C for 1 hour to evaporate the organic binder. These films were used for the determination of IV characteristics and electrical conductivity.

The I-V characteristics of films of CaTiO₃, PbTiO₃ and ZnTiO₃ at room temperature are depicted in Fig. 2.6C (a). Here voltage was continuously varied with constant room temperature and change in conductance was recorded. I-V characteristics are observed to be symmetrical in nature, indicating the ohmic nature of nanocrystalline materials.

Electrical conductivities for synthesized materials are shown in Fig. 2.6C (b) Electrical performance of the material was studied by measuring change in conductance with temperature. The dependence of conductivity of metal titanate films in air ambience. The conductivity of the film goes on increasing with increase in temperature, indicating negative temperature coefficient (NTC) of resistance. This shows the semiconducting nature of the materials.

Figure 2.6C (b) depicts the variation of electrical conductivity as a function of temperature. Activation energies were estimated from the slope of log $\sigma$ versus 1/T curve. Activation energies obtained for CaTiO₃, ZnTiO₃ and PbTiO₃ are found to be 0.757 kJ/mole, 0.946 kJ/mole and 1.176 kJ/mole respectively (Table 2.5C). The observed trend is explained on the basis of ionic size of Ca, Zn and Pb. The trend in observed activation energy is in reverse order of ionic radii. Smaller ion carries more current and hence shows decrease in activation energy.
Fig. 2.6C: a) I-V Characteristic of CTiO$_3$, and b) electrical conductivity of CTiO$_3$. 

(a)

(b)