4. RESULTS AND DISCUSSION

4.1 MWO₄ (M= Ca, Ba, Sr, Pb and Cd):

Metal tungstates with large bivalent cations like Ca²⁺, Sr²⁺, Ba²⁺ and Pb²⁺ tend to crystallize in Scheelite type tetragonal structure where with metal ions of smaller cation radii such as Zn²⁺, Fe²⁺, Co²⁺, Ni²⁺ and Cd²⁺ tungstates crystallize in Wolframite type structure.

Fig.4.1 shows XRD patterns of (a) physical unground mixture of stoichiometric amounts of BaCl₂ and Na₂WO₄, (b) mixture after grinding for half an hour in an agate mortar at room temperature and after washing with water. XRD pattern shown in Fig.4.1(a) for the unground mixture of BaCl₂+Na₂WO₄ shows peaks characteristic of the reactants BaCl₂ and Na₂WO₄, while all the peaks in XRD pattern depicted in Fig.4.1(b) for the same mixture after grinding and washing could be indexed as due to BaWO₄ of JCPDS card Number (43- 0646) with no extra peaks due to NaCl or reactants as impurity suggesting that metathetic reaction is induced by grinding the reactants together.

Recently, Chang Sung Lim [2] reported formation of BaWO₄ using a solid state metathetic route assisted by cyclic microwave irradiation with subsequent heat treatment at 600°C for 3hrs. Cavalcante [3] also reported formation of BaWO₄ powders by co-precipitation and microwave processing at 413K. The room temperature solid state metathetic synthesis reported in the present study is the lowest temperature so far reported for the synthesis of BaWO₄ powders.
Fig. 4.1 XRD patterns of  
a) unground stoichiometric mixture of BaCl₂+Na₂WO₄  
b) stoichiometric mixture of BaCl₂+Na₂WO₄ ground and washed with water.

Fig.4.2 depicts XRD patterns of resultant powders obtained from respective stoichiometric mixtures of MCl₂ (M=Ca, Sr and Pb) and Na₂WO₄ ground at room temperature for half an hour followed by washing with distilled water. These XRD patterns agree well with the respective JCPDS data for CaWO₄, SrWO₄ and PbWO₄ [JCPDS card No for CaWO₄:77-2234; for SrWO₄: 08-0490; for PbWO₄ :85-1857] and showed no extra peaks indicating that samples are phase pure. Unit Cell parameters calculated using TJB Holland & SAT Redfern 1995 software from XRD data of these samples are given in Table 4.1. Zalga [4] reported synthesis of calcium and barium tungstates by aqueous sol-gel method using tartaric acid as complexing agent and heating the xerogel obtained at 500°C for 1hr with subsequent annealing at 800°C for 1hr. Sulawan KaowPhong et al [5] reported formation of nanostructured CaWO₄ by
solvothermal synthesis at a temperature of 160°C for 6h, using Ca(NO$_3$)$_2$4H$_2$O and Na$_2$WO$_4$.2H$_2$O as precursors. Xiufeng Zhao [6] developed a procedure for SrWO$_4$ via a precipitation reaction between SrCl$_2$ and Na$_2$WO$_4$ in presence of polymethacrylic acid. The procedure reported in the present paper for the synthesis of Ca, Sr, Ba, Pb and Cd tungstates is simple, cost effective, operational at ambient temperature and requires no further annealing as required for samples prepared by using microwave energy or hydrothermal bombs.

**Fig. 4.2** XRD Patterns of MCl$_2$ + Na$_2$WO$_4$ ground for 30 minutes and washed with water, M is a) Ca b) Sr and c) Pb.
Table 4.1 Calculated Lattice parameters of Ca, Sr, Ba, Pb tungstates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice Parameters calculated in (Å)</th>
<th>Lattice Parameters from JCPDS in (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>CaWO₄</td>
<td>5.21540</td>
<td>11.31500</td>
</tr>
<tr>
<td>SrWO₄</td>
<td>5.43764</td>
<td>11.99367</td>
</tr>
<tr>
<td>BaWO₄</td>
<td>5.58568</td>
<td>12.65862</td>
</tr>
<tr>
<td>PbWO₄</td>
<td>5.44111</td>
<td>12.02770</td>
</tr>
</tbody>
</table>

Fig. 4.3 depicts XRD patterns of ground mixture obtained from stoichiometric quantities of CdCl₂ and Na₂WO₄ followed by washing with distilled water and drying in an air oven. Though all the XRD peaks in Fig 4.3(a) are indicative of the formation of CdWO₄ at room temperature, since the peaks are broad indicating nano range sample particles, it is subjected to heat treatment at 600°C for 3hrs to improve crystallization and obtain sharper peaks that could be indexed unambiguously. XRD pattern of the heat treated sample shown in Fig. 4.3(b) agreed well with that of CdWO₄ (JCPDS card Number 14-0676). The indexing confirmed that CdWO₄ was formed at room temperature.
Formation of CaWO$_4$, SrWO$_4$, BaWO$_4$, PbWO$_4$ was further studied by Raman spectroscopy and the obtained spectra given in Fig 4.4 are in good agreement with the literature data [7]. The vibrational modes in the Raman spectrum of CaWO$_4$, SrWO$_4$, BaWO$_4$, PbWO$_4$ are classified into two groups, internal and external [8]. The internal vibrations are related to the [WO$_4$]$^{2-}$ molecular group with a stationary mass center. The external vibrations or lattice phonons are associated with the motion of the Ca$^{2+}$(or) Sr$^{2+}$(or) Ba$^{2+}$(or) Pb$^{2+}$ cation and rigid molecular units. In the free space, [WO$_4$]$^{2-}$ tetrahedral show T$_d$-symmetry. The Raman modes for the CaWO$_4$, SrWO$_4$, BaWO$_4$, PbWO$_4$ are shown in the fig.4.4 were detected as $\nu_1$ ($A_g$), $\nu_3$ ($B_g$), $\nu_3$ ($E_g$), $\nu_4$ ($E_g$), $\nu_4$ ($B_g$), and $\nu_2$ ($B_g$) vibrations at 920, 836, 798, 371, 334 and 235 cm$^{-1}$, respectively, which provide evidence of a scheelite structure. The well resolved sharp peaks for the
CaWO₄, SrWO₄, BaWO₄, PbWO₄ indicate that the synthesized particles are highly crystallized. A free rotation mode was detected at 187 cm⁻¹ and external modes were localized at 133 cm⁻¹. This result is in agreement with that reported in the literature [9]. The internal vibration mode frequencies exhibited a dependence on the lattice parameters and the degree of the partially covalent bond between the cation and molecular ionic group [WO₄]²⁻. The type of cations (Ca²⁺, Sr²⁺ Ba²⁺) can influence the Raman modes by changing the size of the crystal unit cell and by a covalent cation effect [8]. There is an essential dependence of the bandwidth of the ν₁ (A₉) Raman mode on the peculiarities of the crystal lattice and the type of M²⁺ cation in the series of MWO₄ (M=Ca, Sr, Ba, Pb) crystals with a scheelite structure. Moving in the series of tungstates Ca²⁺, Sr²⁺ Ba²⁺ increases the unit cell and interionic distance inside the molecular group. The extent of covalency bond between the cation and molecular group usually decreases within the series Ca²⁺, Sr²⁺ Ba²⁺[2].

![Raman Spectra](image.png)

Fig. 4.4  Raman Spectra of (a) CaWO₄ (b) SrWO₄ (c) BaWO₄ (d) PbWO₄ at room temperature.
Fig 4.5. shows the Raman spectra of CdWO₄ at room temperature. The vibration modes in the Raman spectra of tungstates are classified into two groups, internal and external [8,10]. The internal vibrations can be explained by the [WO₆]⁶⁻ molecular group with a stationary mass center. The external vibrations or lattice phonons are associated to the motion of the Cd²⁺ cation and rigid molecular units. The internal Raman modes for the CdWO₄ particles in Fig.4.5 were detected at 898, 773, 688, 549, 388 and 307 cm⁻¹. The free rotation modes were detected at 248, 230 cm⁻¹ and the external modes were localized at 178-117 cm⁻¹. Further the well resolved peaks obtained in this study agree well with the internal Raman modes, free rotation modes and external modes reported by Chang Sung Lim [11]. Chang Sung Lim [11] synthesized well crystalline monoclinic wolframite type CdWO₄ using cyclic microwave irradiation followed by subsequent heat treatment at 600⁰C for 3hrs. Recently Sofronor et al [12] reported microwave synthesis of CdWO₄ using Cd(NO₃)₂ and ammonium tungstates as precursors. According to these investigators CdWO₄ Scheelite phase exists upto 200⁰C and thereafter transforms to monoclinic structure.
Fig. 4.5 Raman spectra of CdWO$_4$.

Fig. 4.6.(a), 4.6(b), 4.6(c), 4.6(d) and 4.6(e) shows SEM micrographs of BaWO$_4$, CaWO$_4$, SrWO$_4$, PbWO$_4$ and CdWO$_4$ powders respectively. As can be seen from the SEM micrographs, BaWO$_4$, CaWO$_4$, SrWO$_4$ and PbWO$_4$ showed no characteristic morphology where as CdWO$_4$ showed a typical morphology with formation of anisotropic particles. From the SEM image, the particle size is estimated to be in the range of micrometer.

Fig. 4.7(a), 4.7(b), 4.7(c), 4.7(d) and 4.7(e) shows EDS of BaWO$_4$, CaWO$_4$, SrWO$_4$, PbWO$_4$ and CdWO$_4$ powders respectively. Elemental analysis of the samples confirms the presence of all elements in the composition of the sample with no extra lines due to any contamination. This further confirms that the byeproduct is completely washed and the product is phase pure.
Fig. 4.6 SEM images of a) BaWO₄ powder b) CaWO₄ powder c) SrWO₄ powder d) PbWO₄ powder e) CdWO₄ powder respectively.
Fig. 4.7 EDS of a) BaWO₄ powder b) CaWO₄ powder c) SrWO₄ powder d) PbWO₄ powder e) CdWO₄ powder respectively.

Fig 4.8 shows the Fourier Transform Infrared spectra of BaWO₄ at room temperature in the wave number range of 400-4000 cm⁻¹. A stretching vibration for BaWO₄ in the figure was detected as a strong W-O stretch in the [WO₄]²⁻ tetrahedral at 816 cm⁻¹. Similar characteristics absorption bands of metal tungstates for the scheelite oxides having S₄ site symmetry in this region have been reported in the literature [13]. The [WO₄]²⁻ is constituted by four internal modes (ν₁ (A₁), ν₂ (E), ν₃ (F₂) and ν₄ (F₂)) specified as symmetric stretching, symmetric bending, asymmetric stretching and
asymmetric bending modes. All these modes are Raman active, whereas only \( \nu_3 (F_2) \) and \( \nu_4 (F_2) \) are IR active [2].

![Graph showing FT-IR spectrum of BaWO\(_4\) at room temperature.](image)

*Fig. 4.8 Fourier Transform Infrared spectrum of BaWO\(_4\) at room temperature*

Fig 4.9 shows the FT-IR spectra of CaWO\(_4\) at room temperature in the wave number range of 400-4000 cm\(^{-1}\). The strong peak at 781 cm\(^{-1}\) is associated with the stretching vibration of the W-O bond in [WO\(_4\)]\(^{2-}\) tetrahedral [5], which is in accord with the detection of tungstates analysed by XRD.
Fig. 4. 9 Fourier Transform Infrared spectrum of CaWO₄ at room temperature

Fig 4.10. shows the FT-IR spectra of SrWO₄ at room temperature in the wave number range of 400-4000 cm⁻¹. The stretching vibration was detected as a strong W-O stretch in the [WO₄]²⁻ tetrahedra at 804 cm⁻¹. Similar characteristics absorption bands of MWO₄ (M = Ba, Ca, Sr) for the scheelite oxides having S₄ site symmetry in this region have been reported in the literature [13]. The [WO₄]²⁻ is constituted by four internal modes (ν₁(A₁), ν₂(E), ν₃(F₂) and ν₄ (F₂)) specified as symmetric stretching, symmetric bending, asymmetric sytreching and asymmetric bending modes [14]. All these modes are Raman active, whereas only ν₃(F₂) and ν₄ (F₂) are IR active.
Fig. 4.11 shows a FTIR spectra of the as-synthesized PbWO$_4$ sample. For T$_d$ symmetry, the vibrations for the [WO$_4$]$^{2-}$ tetrahedral units are $\Gamma_{T_d} = A_1(\nu_1) + E(\nu_2) + F_2(\nu_3) + F_2(\nu_4)$. Only the $F_2(\nu_3, \nu_4)$ modes are IR active for the vibration stretching in the [WO$_4$]$^{2-}$ tetrahedrons [15-17]. Therefore, a strong WO stretching in [WO$_4$]$^{2-}$ tetrahedrons was detected at 767 cm$^{-1}$. 

Fig. 4.10. Fourier Transform Infrared spectrum of SrWO$_4$ at room temperature
Fig. 4.11. Fourier Transform Infrared spectrum of PbWO₄ at room temperature

Fig. 4.12 shows FT-IR spectra of CdWO₄ at room temperature in the wave number range of 400-4000 cm⁻¹. The bending and stretching vibrations of Cd-O (531 cm⁻¹), W-O (617, 632, 642 cm⁻¹) and Cd-O-W (714, 823 cm⁻¹) were identified in the synthesized CdWO₄. These results are in agreement with the literature.[11,12,18].
The above results clearly demonstrate that the solid-state metathetic synthesis route yields phase pure BaWO₄, CaWO₄, SrWO₄, PbWO₄ and CdWO₄ at room temperature without making use of oxide precursors and without subjecting the reaction mixture to microwave energy or thermal energy.
4.2 MWO$_4$ (M= Fe, Mn, Co, Ni and Zn):

Thermograms of homogenised mixtures of MCl$_2$ + Na$_2$WO$_4$. 2H$_2$O are shown in Figures 4.13 to 4.17. in the temperature range of ambient to 1000$^\circ$C for a heating rate of 10$^\circ$C/min. All thermograms indicate might loss upto about 300$^\circ$C followed by a plateau upto 600-700$^\circ$C. Thereafter there is another weight loss. The first weight loss may be ascribed to loss of water from Na$_2$WO$_4$ while the second weight loss may correspond to decomposition of product formed. Hence, the heat treatment of 400$^\circ$C is fixed for all the samples for solid-state methathesis reaction.

Thermogram of the homogenised mixture of MnCl$_2$.4H$_2$O + Na$_2$WO$_4$. 2H$_2$O in 1:1 mole ratio is shown in Fig. 4.13.
Fig. 4.13. Thermogram of homogenised mixture of MnCl$_2$.4H$_2$O + Na$_2$WO$_4$.2H$_2$O in the 1:1 mole ratio from room temperature to 1000$^\circ$C.
Thermogram of the homogenised mixture of FeCl$_2$ + Na$_2$WO$_4$. 2H$_2$O in 1:1 mole ratio is shown in Fig. 4.14.

*Fig. 4.14. Thermogram of homogenised mixture of FeCl$_2$ + Na$_2$WO$_4$. 2H$_2$O in the 1:1 mole ratio from room temperature to 1000°C.*
Thermogram of the homogenised mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in 1:1 mole ratio is shown in Fig. 4.15.

![Thermogram of homogenised mixture of CoCl$_2$.$6$H$_2$O + Na$_2$WO$_4$.2H$_2$O in the 1:1 mole ratio from room temperature to $1000^\circ$C.](image)

Fig. 4.15. Thermogram of homogenised mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in the 1:1 mole ratio from room temperature to $1000^\circ$C.
Thermogram of the homogenised mixture of NiCl$_2$.6H$_2$O + Na$_2$WO$_4$. 2H$_2$O in 1:1 mole ratio is shown in Fig. 4.16.

Fig. 4.16. Thermogram of homogenised mixture of NiCl$_2$.6H$_2$O + Na$_2$WO$_4$. 2H$_2$O in the 1:1 mole ratio from room temperature to 1000$^\circ$C.
Thermogram of the homogenised mixture of ZnCl$_2$ + Na$_2$WO$_4$. 2H$_2$O in 1:1 mole ratio is shown in Fig. 4.17.

*Fig. 4.17. Thermogram of homogenised mixture of ZnCl$_2$ + Na$_2$WO$_4$. 2H$_2$O in the 1:1 mole ratio from room temperature to 1000$^\circ$C.*
XRD patterns obtained for homogenised mixtures of MCl₂ + Na₂WO₄ (where M= Mn, Fe, Co, Ni and Zn) subjected to heat treatment at 400ºC for 4hrs followed by washing with water until free from chloride and dried are given in Figures 4.18 to 4.21. XRD patterns of homogenised mixture of NiCl₂ + Na₂WO₄ at room temperature and heat treated at 300ºC and 400ºC for 4hrs followed by washing are shown in Fig.4.18. XRD patterns indicate formation of well crystalline NiWO₄ only for the sample heat treated at 400ºC for 4hrs. All the peaks in the XRD pattern could be indexed as the observed pattern is in good agreement with that of NiWO₄ given in JCPDS file no.15-0755. No extra peaks were noticed which indicates the formation of phase pure sample. Observed XRD patterns below 400ºC does not match with the highest intensity peaks of NiCl₂, Na₂WO₄ and NaCl. Hence these peaks may be ascribed to amorphous precursor with some partially crystalline NiWO₄,((002), (022) and (220) peaks).

Fig. 4.18. XRD patterns of stoichiometric mixture of NiCl₂ + Na₂WO₄ ground for 2hrs a) room temperature b) heat treated at 300ºC for 4hrs c) heat treated at 400ºC for 4hrs and washed free of chloride.
Fig 4.19 shows the XRD patterns of homogenised mixture of stoichiometric amounts of 
ZnCl₂ and Na₂WO₄, ground for 2 hrs at room temperature and subjected to heat 
treatment of 400°C for 4hrs, both washed free of chloride and dried. The washed 
product of ZnWO₄ at room temperature did not indicate any sharp peaks characteristic 
of the reactants or NaCl bye product. The broad peak coincides with the 100% intensity 
peak of ZnWO₄ and this can be attributed to ZnWO₄ in the amorphous form. However, 
when subjected to heat treatment at 400°C, characteristic peaks due to formation of 
well crystalline phase pure ZnWO₄ were obtained and the data is in agreement with 
that reported in JCPDS file no.73-0554.

![XRD patterns](image)

**Fig. 4.19. XRD patterns of stiochiometric mixture of ZnCl₂ + Na₂WO₄ ground for 
2hrs a) room temperature, b) heat treated at 400°C for 4hrs.**
Fig. 4.20. shows the XRD patterns obtained for mixtures of \( \text{MnCl}_2 + \text{Na}_2\text{WO}_4 \) and \( \text{CoCl}_2 + \text{Na}_2\text{WO}_4 \) ground for 2hrs and heated at 400°C for 4hrs followed by washing to remove NaCl. The observed XRD patterns are in good agreement with the reported data for MnWO\(_4\) and CoWO\(_4\) of JCPDS files 80-0134 and 72-0479 respectively. Miroslaw Maczka et al [19] reported two different synthesis routes for MnWO\(_4\) (i) a hydrothermal method using ethanolamine and CTAB and (ii) by annealing a precursor obtained by co-precipitation. In their second method, XRD patterns were indicative of nanocrystalline MnWO\(_4\) formation with crystallite size smaller than 20 and 26 nm when the synthesis was performed at 250 and 400°C, respectively. In the present method sharp peaks characteristic of large and well crystallized MnWO\(_4\) particles were revealed for annealing at 400°C for 4 hrs.

![XRD patterns](image)

**Fig. 4.20 XRD patterns of stoichiometric mixture of a) \( \text{MnCl}_2 + \text{Na}_2\text{WO}_4 \) ground for 2hrs and heat treated at 400°C for 4hrs washed and dried. b) \( \text{CoCl}_2 + \text{Na}_2\text{WO}_4 \) ground for 2hrs, heat treated at 400°C at 4hrs washed and dried.**
Fig 4.21 shows the XRD patterns obtained for mixture of FeCl$_2$+Na$_2$WO$_4$ ground for 2hrs and heat treated at 400°C for 2hrs and at 600°C for 3hrs and washed free from NaCl bye product. Though the formation of FeWO$_4$ is evident at 400°C, for unambiguous indexing of peak positions, the sample is subjected to heat treatment at 600°C for 3hrs to render it more crystalline. All peaks for the resultant sample could be indexed in accordance with JCPDS file no. 71-2391.

Synthesis of MWO$_4$ powders was reported by solution based metathesis reaction using equimolar solutions of metal nitrates and sodium tungstate, with subsequent heating of the precipitate to 800°C for 15hr [20]. Parhi et al [21] reported synthesis of ZnWO$_4$, NiWO$_4$ and MnWO$_4$ by microwave assisted solid-state metathesis using 2.45 GHz microwave frequency and a power of 1100 W for 10 minutes duration. Though crystalline ZnWO$_4$ was obtained at room temperature by this process, crystalline MnWO$_4$ and NiWO$_4$ were obtained only after heat treatment at 500°C for 6hrs. Angana sen et al [22] reported the synthesis of Co, Ni, Cu and Zn metal tungstates from the complete evaporation of polymer based metal-complex precursor solution subjected to heat treatment. Rajagopal [23] reported the hydrothermal synthesis of FeWO$_4$ and CoWO$_4$ using sodium tungstate with ferrous ammonium sulphate and cobalt chloride solutions as precursors respectively. Recently Garcia-Perez et al [24] reported the synthesis of Co, Cu, Mn and Ni tungstates by co-precipitation method at 400°C. Tiziano Montini et al [25] reported the synthesis of transition metal tungstates M$^{ll}$WO$_4$ (M = Co$^{ll}$, Ni$^{ll}$, Cu$^{ll}$, Zn$^{ll}$) by reaction of transition metal nitrates with sodium tungstates and then subjected to heat treatment at 500°C. The SSM synthesis reported in the present study is the lowest synthesis temperature reported for solid-state synthesis. It is less cumbersome and could be performed at ambient pressure.
Fig. 4.21. XRD patterns of stoichiometric mixture of FeCl₂ + Na₂WO₄ ground for 2hrs and heat treated at a) 400°C for 4hrs b) 600°C for 3hrs and washed free of chloride.

Fig 4.22. shows Raman spectra of MnWO₄, FeWO₄, CoWO₄, NiWO₄ and ZnWO₄. In terms of group theoretical analysis, wolframite structure belonging to P2/c (z = 2) monoclinic structure is expected to give 18 (8AG + 10BG) Raman-active bands out of 36 possible lattice modes [26]. Raman spectra for all samples revealed peaks due to 8AG (breathing of tungstate tetrahedra) vibrations while some peaks due to 10BG were not resolved. Based on the previous reports, the most intense band in ZnWO₄ was ascribed to antisymmetric bridging mode associated with the tungsten chain [27]. In MnO₄ the band at 127 cm⁻¹ accompanied by two weak bands in the range 160 and 180 cm⁻¹ were
ascribed to interchain deformation and torsion modes [14]. Our data is in agreement with those reported earlier [26],[27],[14].

Fig. 4.22. Raman spectra of MnWO₄, CoWO₄, NiWO₄ and ZnWO₄ heat treated at 400°C and FeWO₄ heat treated at 600°C.

Fig. 4.23(a), 4.23(b), 4.23(c), 4.23(d) and 4.23(e) shows SEM micrographs of MnWO₄, FeWO₄, CoWO₄, NiWO₄ and ZnWO₄ powders respectively. As can be seen from the SEM micrographs, MnWO₄, FeWO₄, CoWO₄ and ZnWO₄ showed no characteristic morphology with particles of different sizes due to aggregation where as NiWO₄ showed a typical morphology with formation of spherical particles. From the SEM image, the particle size is estimated to be in the range of micrometer.
Fig. 4.24(a), 4.24(b), 4.24(c), 4.24(d) and 4.24(e) shows EDS of MnWO$_4$, FeWO$_4$, CoWO$_4$, NiWO$_4$ and ZnWO$_4$ powders respectively. Elemental analysis of the samples confirms the presence of all elements in the composition of the sample with no extra lines due to any contamination.

Fig. 4.23. SEM images of a) MnWO$_4$ powder b) FeWO$_4$ powder c) CoWO$_4$ powder d) NiWO$_4$ powder and e) ZnWO$_4$ powder respectively.
Fig. 4.24. EDS of a) MnWO$_4$ powder b) FeWO$_4$ powder c) CoWO$_4$ powder
d) NiWO$_4$ powder and e) ZnWO$_4$ powder respectively.

Fig. 4.25. shows the Fourier Transform Infrared spectrum of MnWO$_4$ in the wave
number range of 400-4000 cm$^{-1}$. Well known MnWO$_4$ absorption peaks in the range
of 500-1000 cm$^{-1}$ were detected, which are similar to that of the bulk IR pattern
previously reported for MnWO$_4$. H$_2$O, where in the inorganic modes lie at the low-
wavenumber end of the spectra [28]. The spectra shows the inorganic modes in the
range of 500–1000 cm$^{-1}$ of the low wavenumber side at 515, 612, 700, 820, 865 and
960 cm$^{-1}$. The vibrations are in accordance with those of other researchers [29]. These bands are assigned to be the internal stretching modes of $\nu_3(A_u)$ and $\nu_3(E_u)$ transitions [30].

Fig. 4.25. Fourier Transform Infrared spectrum of MnWO$_4$.  

Fig.4.26 shows the Fourier Transform Infrared spectrum of FeWO$_4$ in the wave number range of 400-4000 cm$^{-1}$. The spectrum shows that there are characteristic absorption peaks at 530, 612, 702, 800 and 950 cm$^{-1}$. The broad bands are similar to those reported for synthetic ferberite, bands of which are shown to occur in another study at 828 and 625 cm$^{-1}$ respectively [31,32]. The absorption bands at 800 and 612 cm$^{-1}$ correspond to the O-W-O vibration mode and W-O stretching band, respectively [33].
Fig. 4.26. Fourier Transform Infrared spectrum of FeWO₄.

Fig. 4.27 shows the FT-IR spectrum of CoWO₄ in the wave number range of 400-4000 cm⁻¹. Intense bands appeared in the low frequency region of 400–1,000 cm⁻¹ which belongs to the characteristic deformation modes of Co–O, W–O and W–O–W bridges [34]. IR spectra below 500 cm⁻¹ could have been due to the deformation modes of W–O bonds in WO₆ octahedra or the deformation of W–O–W bridges [35]. The bands positioned at 820 cm⁻¹ and 621 cm⁻¹ were associated to the O–W–O vibration mode and the W–O bond stretching, respectively [36,32]. The strong intense band in the region of 3,000–3,800 cm⁻¹ corresponds to OH stretching vibration of surface absorbed or internally bonded water molecules [37]. The bending mode of H–O–H is located at about 1,640 cm⁻¹. The data reported in this thesis well agreed with the literature [38].
Fig. 4.27. Fourier Transform Infrared spectrum of CoWO$_4$.

Fig.4.28 shows the FT-IR spectrum of NiWO$_4$ in the wave number range of 400-4000 cm$^{-1}$. For wolframite, the total representation of the P2/c unit cell contains 18 Raman-active modes ($8A_g+10B_g$), 15 infrared-active modes ($7A_u+8B_u$), and 3 acoustic vibrational modes ($A_u+2B_u$) [39,40]. The wolframite structure is constituted by WO$_6$ polyhedra, with a dense packing of these coordination polyhedral in the unit cell. The tungstate ions are additionally connected to each other by means of intermolecular interactions of the W$^6_0$W type. The characteristic vibrational bands corresponding to this structural fragment appear at the 500–700 and 220–280 cm$^{-1}$ regions and are assigned to stretching and bending modes of the W$^6_0$W unit, respectively [41,42]. Further the spectrum is well agreed with literature [43].
Figure 4.29 shows FT-IR spectrum of ZnWO₄ in the wavenumber region of 400-4000 cm⁻¹, which reveals bands at 472 cm⁻¹ and 518 cm⁻¹ that are due to bending and stretching vibrations of Zn-O and further there are two more peaks located at 669 and 742 cm⁻¹ which originated from bending and stretching vibrations of W-O. There also exits a band at 846 cm⁻¹ that arises from bending and streching vibrations of Zn-O-W [44]. Weaker band near 3600 cm⁻¹ and 1600 cm⁻¹ are due to the O-H stretching and the H-O-H bending vibrations, respectively [45]. The data well agreed with the literature data [46-49].
Fig. 4.29 Fourier Transform Infrared spectrum of ZnWO₄.
4.3 Barium stannate and Barium zirconate:

X-ray diffraction patterns obtained for the stoichiometric and homogenized solid mixture of BaCl$_2$ and Na$_2$SnO$_3$ subjected to heat treatment at 600$^\circ$C for 8 hours and 800$^\circ$C for 4 hours respectively, followed by washing with water to remove the byproduct NaCl are shown in Fig.4.30. The observed XRD pattern in Fig.4.30(a) did not show the formation of BaSnO$_3$ through metathetic exchange. However in the XRD pattern depicted in Fig.4.30(b), all the observed peaks could be indexed since they are in complete agreement with reported XRD pattern of BaSnO$_3$ (JCPDS card no 15-0780) indicating the formation of crystalline phase pure BaSnO$_3$. There are no extra peaks either due to SnO$_2$ or Ba$_2$SnO$_4$ contamination. Traditional solid-state synthesis of BaSnO$_3$ requires temperatures of the order of 1200$^\circ$C for solid state reaction between BaCO$_3$ and SnO$_2$. Azad et al. [50] reported the synthesis of BaSnO$_3$ via self heat-sustained reaction technique in which they heated Ba(NO$_3$)$_2$ with metallic tin powder at 1100$^\circ$C for 12 hours which showed the presence of Ba$_2$SnO$_4$ along with BaSnO$_3$ and formation of phase pure BaSnO$_3$ was achieved only by further heating of calcinated mixture at 1200$^\circ$C for 24 hours. Aguas et al. [51] reported self propagating high temperature synthesis (SHS) of BaSnO$_3$ from barium peroxide and different tin sources like Sn, SnCl$_2$ and SnO$_2$. According to these investigators, the product at 950-1050$^\circ$C was predominantly BaSnO$_3$ with some SnO$_2$ and Ba$_2$SnO$_4$ impurities. Annealing of SHS powders at 1000$^\circ$C for 2 to 72 hours formed phase pure BaSnO$_3$. Shail upadhyay et al. [52] reported synthesis of BaSnO$_3$ using BaCO$_3$ and SnO$_2$ by calcination at 1475K for 6 hours followed by sintering at 1525K for 6 hours. Koferstein et al. [53] reported the synthesis of nano-sized BaSnO$_3$ from barium tin 1,2-ethane diolato complex precursor by a rate controlled calcination process at 820$^\circ$C. The solid
The state metathesis method reported in the present paper is much simpler and required lower temperature compared to previously reported methods.

**Fig. 4.30.** XRD patterns of a) mixture of BaCl$_2$+Na$_2$SnO$_3$ ground for 4hrs and heat treated at 600$^\circ$C 8hrs b) 800$^\circ$C 4hrs and washed with water until it is free from NaCl.

Thermogram of the washed and dried precipitate obtained from the mixture of aqueous solutions of ZrO(NO$_3$)$_2$, KCl and oxalic acid is given in Fig.4.31. Thermogravimetric curve shows a total weight loss of 47.5% in the temperature region between 50 to 550$^\circ$C followed by a plateau with no intermediate in between. Based on the experimental weight loss observed, molecular formula of the precipitate is assigned as
K₂[ZrO(C₂O₄)₂].3H₂O. Theoretical weight loss of 46.2% for the complex with the following decomposition pattern agrees well with the observed weight loss.

\[
\text{K}_2[\text{ZrO(C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O} \rightarrow \text{K}_2\text{O} + \text{ZrO}_2 + 2\text{CO}_2 + 2\text{CO} + 3\text{H}_2\text{O}
\]

Differential thermal analysis (DTA) curve of the precipitate showed two broad endothermic peaks in the temperature range of 50⁰ to 200⁰C and 220⁰-500⁰C. These two peaks can be assigned to dehydration and decomposition respectively. The lattice parameters obtained by using Unit Cell parameters calculated using TJB Holland & SAT Redfern 1995 software for these samples are given in Table.4.2

![Fig. 4.31. TG and DTA of K₂[ZrO(C₂O₄)₂].](image)
Table 4.2
Calculated Lattice parameters of BaSnO$_3$ and BaZrO$_3$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice Parameters calculated (Å$^0$)</th>
<th>Lattice parameters from JCPDS$^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>BaSnO$_3$</td>
<td>4.11876</td>
<td>4.1163</td>
</tr>
<tr>
<td>BaZrO$_3$</td>
<td>4.18792</td>
<td>4.193</td>
</tr>
</tbody>
</table>

$^8$JCPDS file no. BaSnO$_3$ 15-0780, BaZrO$_3$ 06-0399.

XRD patterns of the stiochiometric and homogenized solid mixture of BaCl$_2$ and K$_2$[ZrO(C$_2$O$_4$)$_2$] heat treated at 600$^0$C for 8hrs and 800$^0$C for 4hrs followed by washing with water are shown in the Fig.4.32. Though the XRD pattern given in Fig 4.32(a) shows the formation of BaZrO$_3$, there are some extra peaks may be due to unreacted reactants. However, all the peaks in Fig 4.32(b) could be indexed to phase pure BaZrO$_3$ (JCPDS File No 06-0399). There are no extra peaks due to contamination. Traditionally, zirconates are synthesized through solid state reaction between ZrO$_2$ and metal carbonates at high temperatures which results in structural inhomogeneity and lack of stoichiometry. Guan Li et al. [54] reported the preparation of Eu$^{3+}$ doped BaZrO$_3$ by solid-state reaction of BaCO$_3$, Zr$_2$O$_3$ and Eu$_2$O$_3$ at 1250-1450$^0$C for 4 hours. Anjali and Malini [55] reported the synthesis of noncrystalline BaZrO$_3$ by a soft solution process coupled with sonication. Aimable et al. [56] reported synthesis of nanocrystalline BaZrO$_3$ using a hydrothermal synthesis process working in supercritical conditions with barium acetate or barium nitrate as a precursor for Ba. Borja-Urby et al. [57] reported the synthesis of pure BaZrO$_3$ and Bi doped BaZrO$_3$ using Barium nitrate and ZrOCl$_2$ as precursors and cetyl trimethyl ammonium bromide.
(CTAB) as dispersing agent and NaOH as precipitating agent. The precipitate obtained from hydrothermal reaction at 100$^\circ$C for 24 hours, on heating for 3hrs at 1000$^\circ$C in atmosphere showed XRD characteristic of BaZrO$_3$. Compared to these reported methods, the solid-state metathetic synthesis proposed in this paper is much simpler to obtain phase pure BaZrO$_3$ at relatively lower temperature compared to other solid-state methods.

Fig. 4.32. XRD patterns of a) mixture of BaCl$_2$ + K$_2$[ZrO(C$_2$O$_4$)$_2$] ground for 4hrs and heat treated at 600$^\circ$C for 8hrs b) 800$^\circ$C for 4hrs and washed with water until it is free from NaCl.

SEM micrograph of the resultant BaSnO$_3$ powder obtained by heat treatment at 800$^\circ$C for 4hours and washed free of NaCl is given in Fig 4.33(a). This indicates particles of varying size in the µm range with no characteristic shape. SEM micrograph of the
resultant BaZrO$_3$ powder obtained by heat treatment at 800°C for 4 hours and washed free of NaCl is given in Fig 4.33(b). The image mostly contains spherical particles of nearly uniform size.

Figure 4.34(a) and 4.34(b) shows the EDS of BaSnO$_3$ and BaZrO$_3$ powder respectively. Elemental analysis of the samples confirms the presence of all elements in the composition of the sample with no extra lines due to any contamination.

Fig. 4.33. a) SEM image of BaSnO$_3$ powder and b) SEM image of BaZrO$_3$ powder.
Fig. 4.34. EDS of a) BaSnO₃ powder b) BaZrO₃ powder.

Fig. 4.35 shows the FTIR spectrum of BaSnO₃ calcined at 800°C for 4hrs. The distinct features of the spectrum are a broad peak observed at 640.36 cm⁻¹ corresponding to BaSnO₃ vibrations. It is the characteristic stretching mode of Sn-O bonds [58]. A broad peak at 3311.77 cm⁻¹ is observed for the powder synthesized. This peak is assigned to the stretching modes of O-H bond [59]. Water may be present due to adsorption by KBr pellets or by BaSnO₃ powders. At 862.18 cm⁻¹ and 1427.32 cm⁻¹, peaks were observed for the powder synthesized. This corresponds to stretching modes of CO₃²⁻. Carbonates, basically BaCO₃ may form due to absorption of CO₂ from
atmosphere during FTIR analysis [60-61]. All the lines of this spectrum agree with reported values from the literature [62-63].

![Fourier Transform Infrared spectrum of BaSnO3.](image)

*Fig. 4.35. Fourier Transform Infrared spectrum of BaSnO3.*

Figure 4.36 shows the Raman spectrum of BaSnO₃ heat treated at 800°C for 4 hours. We can observe a strong peak at 1060 cm⁻¹ which can be associated to the barium carbonate phase [64]. Previous reported results show that pure BaCO₃ decomposes above temperatures of 1200°C [65]. The presence of trace amounts of BaCO₃ can be seen in the samples heated at 800°C due to their high sensitivity, which could not be detected by XRD. The absence of these peaks at temperature higher than 1200°C will takes place because decomposition of BaCO₃ takes place at temperature above 1200°C as seen in the literature. Rest of that, the results are in agreement with the literature [66].
Figure 4.36. Raman spectrum of BaSnO₃ powder heat treated at 800°C for 4hrs.

Figure 4.37 shows the FTIR spectra of BaZrO₃ heat treated at 800°C for 4hrs. The large vibration observed around 533 cm⁻¹ in the calcined powder is due to Zr-O vibration in the perovskite structure [67]. An absorption band around 3749 cm⁻¹ appeared in the IR spectra are the characteristic of absorbed water. Around 1420 cm⁻¹ absorption band reveal the existence of carbonate (CO₃²⁻) [68]. As FTIR is highly sensitive technique than XRD the peak due to BaCO₃ could not be detected in XRD but found in FTIR. As the decomposition of BaCO₃ takes place above 1200°C and from the FTIR results, it seems that calcination at temperature higher than 800°C is needed to successfully eliminate the carbonate materials. Rest of that, our data is in agreement with the literature [69].
Fig. 4.37. Fourier Transform Infrared spectrum of BaZrO$_3$. 
4.4 MFeO$_3$ Ferrates (M=La & Bi):

As an extension of the above work the synthesis of LaFeO$_3$ and BiFeO$_3$ was undertaken presuming feasibility of metathesis between the MCl$_3$ (M= La, Bi) and K$_3$[Fe(C$_2$O$_4$)$_3$]. 3H$_2$O precursors. However, contrary to the expectation decomposition preceeded metathesis reaction in this case as evidenced by thermoanalytical study.

Thermogram of the homogenised mixture of LaCl$_3$ and K$_3$[Fe(C$_2$O$_4$)$_3$] in 1:1 mole ratio is shown in Fig.4.38 which showed a continuous weight loss upto 850$^0$C and the total weight loss, upto 850$^0$C corresponds to 57%. The experimentally observed weight loss can be ascribed to the following reactions, occurring either in succession or simultaneously in the temperature range of 50$^0$ to 850$^0$C.

\[ \text{LaCl}_3 \cdot 7\text{H}_2\text{O} \rightarrow \text{LaCl}_3 + 7\text{H}_2\text{O} \]

\[ \text{K}_3[\text{Fe(C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O} \rightarrow \text{K}_3[\text{Fe(C}_2\text{O}_4)_3] + 3\text{H}_2\text{O} \]

\[ 2 \text{K}_3[\text{Fe(C}_2\text{O}_4)_3] \rightarrow 3 \text{K}_2\text{O} + \text{Fe}_2\text{O}_3 + 6\text{CO}_2 + 6\text{CO} \]

allowing the overall reaction after decomposition to facilitate the formation of LaFeO$_3$ as per the following equation.

\[ \text{LaCl}_3 \cdot 7\text{H}_2\text{O} + \text{K}_3[\text{Fe(C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O} \rightarrow \text{LaFeO}_3 + 10\text{H}_2\text{O} + 3\text{CO}_2 + 3\text{CO} + 3\text{KCl} \]

for which the theoretical weight loss is 55%. Since the observed weight loss of 57% agrees with the theoretical weight loss, the product expected above 850$^0$C must be LaFeO$_3$. 

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Fig. 4.38 Thermogram of homogenised mixture of LaCl$_3$ and K$_3$[Fe(C$_2$O$_4$)$_3$] in the 1:1 mole ratio from room temperature to 950$^\circ$C.

In order to confirm the formation of LaFeO$_3$, the original well ground mixture of LaCl$_3$ and K$_3$[Fe(C$_2$O$_4$)$_3$] is subjected to heat treatment at 600$^\circ$C and 1000$^\circ$C for 8 hrs and 2 hrs respectively. X-ray diffraction patterns obtained for the heat treated samples washed with water to remove expected byproduct KCl are shown in Fig. 4.39. XRD pattern in Fig 4.39(a) did not show the formation of LaFeO$_3$ where as in the XRD pattern shown in Fig 4.39(b), all the observed peaks could be indexed due to LaFeO$_3$ of JCPDS card no. 37-1493. Since all the observed diffraction peaks are in good agreement with that of LaFeO$_3$ and since there are no extra peaks either due to contamination or due to unreacted precursors, the formation of phase pure LaFeO$_3$ is confirmed.
Synthesis of LaFeO$_3$ has also been reported in literature from the heteronuclear bimetallic complex precursor La[Fe(CN)$_6$].5H$_2$O prepared from mixing the aqueous solutions of La(NO$_3$)$_3$, K$_3$[Fe(CN)$_6$] and thermal decomposition of the complex precursor yielded LaFeO$_3$ at 620$^0$C [70]. The fact that stoichiometric solid-state mixture of LaCl$_3$ and K$_3$[Fe(C$_2$O$_4$)$_3$] on heating yielded LaFeO$_3$ at elevated temperatures coupled with the literature report of the thermal decomposition of La[Fe(CN)$_6$] we thought whether a solid-state stoichiometric mixture of LaCl$_3$ and K$_3$[Fe(CN)$_6$] will also yield LaFeO$_3$, following solid-state metathesis reaction pathway. Conforming to our expectation, the solid mixture of LaCl$_3$ and K$_3$[Fe(CN)$_6$] in 1:1 mole ratio when heat treated at 600$^0$C for 4 hrs followed by washing with water to remove KCl byeproduct yielded LaFeO$_3$ as observed from XRD shown in Fig. 4.39(c) which is well in agreement with that of LaFeO$_3$ of JCPDS card no 37-1493. The net result indicates that formation of phase pure LaFeO$_3$ could be achieved even from physical mixture of precursors which avoids preparation of complex precursor La[Fe(CN)$_6$].5H$_2$O from the aqueous solutions of the reactants.
Fig. 4.39. XRD patterns of 1:1 ground mixtures of LaCl$_3$ and K$_3$[Fe(C$_2$O$_4$)$_3$] heat treated at (a) 600$^{\circ}$C for 8hrs (b) 1000$^{\circ}$C for 2 hrs and (c) mixture of LaCl$_3$ and K$_3$[Fe(CN)$_6$] heat treated at 600$^{\circ}$C for 2hrs.

Fig. 4.40 depicts the XRD pattern obtained for the stoichiometric well-ground mixture of BiCl$_3$ and K$_3$[Fe(C$_2$O$_4$)$_3$] in the mole ratio of 1:1, heat treated at 600$^{\circ}$C for 8 hrs and 800$^{\circ}$C for 4 hrs followed by washing with water. XRD pattern shown in fig 4.40(a) did not indicate the formation of BiFeO$_3$ since the diffraction peaks observed at 2$\theta$ = 28, 52, and 67$^{\circ}$ are correspond to the reactants. Where as, all the peaks in the XRD pattern in fig.4.40(b) could be indexed to BiFeO$_3$ (JCPDS Card no. 86-1518). The absence of any extra peaks either due to contamination or due to unreacted precursors confirm the formation of phase pure BiFeO$_3$. Formation of BiFeO$_3$ has also been reported in literature from the thermal decomposition of the bimetallic complex precursor.
Bi[Fe(CN)₆] at 600-650°C between 5 and 10 hrs. As in the case of LaFeO₃, formation of BiFeO₃ from the heat treatment of a physical mixture of BiCl₃ and K₃[Fe(CN)₆] is also investigated, but unlike LaFeO₃, there is no evidence of formation of BiFeO₃ even upto 800°C.

Fig. 4.40. XRD patterns of 1:1 ground mixtures of BiCl₃ and K₃[Fe(C₂O₄)₃] heat treated at (a) 600°C for 8hrs (b) 800°C for 4hrs.

Fig.4.41 shows the FT-IR spectra of BiFeO₃. The bands at 3600 cm⁻¹ are due to the ν(OH) of the lattice water molecule. Intense bands around 1650 cm⁻¹ corresponds to the ν_asym (C=O) of coordinated oxalate. The bands in the zone of 1320-1420 cm⁻¹ is attributed to ν_sym (C=O) of coordinated oxalate [71]. Specifically, the strong absorptive peaks at 400-600 cm⁻¹ was attribute to the Fe-O stretching and bending vibration, being characteristics of the octahedral FeO₆ groups in the perovskite compounds [72]. Further the data is in agreement with the results of the literature [73-74].
Figure 4.42 shows the FT-IR spectrum of LaFeO₃. There are two strong absorptive bands at about 570 and 400 cm⁻¹ which correspond to Fe-O stretching vibration and O-Fe-O bending vibration of perovskite LaFeO₃, respectively [75-77]. This finding proves the formation of the perovskite LaFeO₃ and is in accordance with the XRD data. Also, in the FT-IR spectrum of LaFeO₃ weak bands were observed in the 1300-1500cm⁻¹ regions which are attributable to carbonate groups [78]. But, these carbonates were not detected by XRD. Therefore, it is concluded that the carbonates the perovskite-type LaFeO₃ by IR are formed on the surface due to exposure to ambient air. The surface of the LaFeO₃ particles obtained from the decomposition of the heteronuclear compound is more active to chemisorptions of gases such as CO₂ in ambient, leading to the formation of the carbonate [78]. Further the data is in agreement with the literature (79-81).
Fig. 4.42. Fourier Transform Infrared spectrum of LaFeO$_3$ obtained at 1000$^\circ$C from LaCl$_3$ and K$_3$[Fe(C$_2$O$_4$)$_3$].

Figure 4.43 shows the FT-IR spectrum of LaFeO$_3$ prepared from mixture of LaCl$_3$ and K$_3$[Fe(CN)$_6$]. The spectrum well agree with the explanation of LaFeO$_3$ above.
Fig. 4.43. Fourier Transform Infrared spectrum of LaFeO₃ obtained at 600°C
from LaCl₃ and K₃[Fe(CN)₆]

The SEM micrographs of LaFeO₃ (from LaCl₃ and K₃[Fe(C₂O₄)₃]), BiFeO₃ (from BiCl₃ and K₃[Fe(C₂O₄)₃]) and LaFeO₃ (from LaCl₃ and K₃[Fe(CN)₆]) respectively are shown in Fig.4.44. SEM micrographs, indicate submicrometer aggregated particles of no characteristic shape.
Fig. 4.44 SEM micrographs of (a) LaFeO₃ obtained at 1000°C from LaCl₃ and K₃[Fe(C₂O₄)₃] (b) BiFeO₃ obtained at 800°C from BiCl₃ and K₃[Fe(C₂O₄)₃] (c) LaFeO₃ obtained at 600°C from LaCl₃ and K₃[Fe(CN)₆].

Figure 4.45(a), 4.45(b) and 4.45(c) shows the EDS of LaFeO₃ (from LaCl₃ and K₃[Fe(C₂O₄)₃]), BiFeO₃ (from BiCl₃ and K₃[Fe(C₂O₄)₃]) and LaFeO₃ from LaCl₃ and K₃[Fe(CN)₆] respectively. Elemental analysis of the samples confirms the presence of all elements in the composition of the sample with no extra lines due to any contamination.
Fig. 4.45. EDS of (a) LaFeO₃ obtained at 1000°C from LaCl₃ and K₃[Fe(C₂O₄)₃] (b) BiFeO₃ obtained at 800°C from BiCl₃ and K₃[Fe(C₂O₄)₃] (c) LaFeO₃ obtained at 600°C from LaCl₃ and K₃[Fe(CN)₆].
4.5. LaVO$_4$ and BiVO$_4$:

In recent years much attention is being paid to the synthesis of nanomaterials because of their interesting properties and potential applications. Most of these techniques are based on bottom up approach. However, if the same phase can be synthesized by solid-state reactions at ambient temperatures, it will be cost effective to obtain the same phase in nanoform by top-down approach as well.

Fig. 4.46. shows the XRD pattern of homogenised mixture of LaCl$_3$ and Na$_3$VO$_4$, after grinding for 2 hours in an agate mortar at ambient temperature followed by washing with water until free from chloride and dried. All the peaks could be indexed to tetragonal zircon type LaVO$_4$ of space group I41/amd and with cell parameters $a=b=7.45687$ Å, $c=6.54123$ Å consistent with literature values (JCPDS Card No: 32-0504). No peaks due to either m-LaVO$_4$ phase or contamination due to unreacted precursors indicates formation of phase pure t- LaVO$_4$.

![XRD pattern](image)

Fig. 4.46. XRD pattern of stoichiometric mixture of LaCl$_3$ + Na$_3$VO$_4$ ground for 2hrs and washed free of chloride.
Fig.4.47 shows the FT-IR spectrum of the solid residue used for XRD studies. A broad absorption band is observed at 786 cm$^{-1}$. t-LaVO$_4$ only generates a broad band in the region of 730-980 cm$^{-1}$, while m- LaVO$_4$ presents several peaks at 783, 802, 821, 836 and 852 cm$^{-1}$[82]. A broad band in the range of 2,800-3,700 cm$^{-1}$ is characteristic of stretching vibrations of O-H bonds of surface absorbed or internally bonded water molecules also reported in literature [83]. The two weaker bands at 1635 and 1369 cm$^{-1}$ can be assigned to the symmetric stretching vibration and bending vibration of the O-H groups, indicating that the as-prepared LaVO$_4$ contains some hydroxyl groups or H$_2$O on their surfaces.

![Fourier Transform Infrared spectrum of the solid residue used for XRD.](image)

*Fig. 4.47. Fourier Transform Infrared spectrum of the solid residue used for XRD.*

Figure 4.48 depicts the XRD pattern of homogenised mixture of BiCl$_3$ and Na$_3$VO$_4$, after grinding for 2 hours in an agate mortar at room temperature followed by washing
with water until free from chloride and dried. All the observed peaks could be indexed due to monoclinic BiVO$_4$ of JCPDS card no. 83-1698. Since all the observed diffraction peaks are in good agreement with that of m-BiVO$_4$ and since there are no extra peaks either due to contamination or due to unreacted precursors, the formation of phase pure BiVO$_4$ is confirmed.

![XRD pattern of stoichiometric mixture of BiCl$_3$ + Na$_3$VO$_4$ ground for 2hrs and washed free of chloride.](image)

*Fig. 4.48. XRD pattern of stoichiometric mixture of BiCl$_3$ + Na$_3$VO$_4$ ground for 2hrs and washed free of chloride.*

Fig. 4.49 shows the FT-IR spectrum of the resultant residue used for XRD at room temperature. The formation of BiVO$_4$ is characterized by a strong absorption band at 754 cm$^{-1}$ [84]. The obvious absorptions at 1623 cm$^{-1}$ and around 3440 cm$^{-1}$ is due to bending and stretching vibrations of the adsorbed H$_2$O molecules, respectively. The data is well in agreement with the literature data [85,86].
Fig. 4.49. Fourier Transform Infrared spectrum of the resultant residue used for X-ray diffraction.

Fig. 4.50(a) and Fig. 4.50(b) shows SEM micrographs of the resultant BiVO₄ and LaVO₄ powders respectively. Fig. 4.50(a) shows that the image mostly contains spherical particles of nearly uniform size where as the image of Fig. 4.50(b) shows no characteristic shape.
Fig. 4.50  a) SEM images of BiVO$_4$ powder and b) SEM image of LaVO$_4$ powder

Figure 4.51(a) and 4.51(b) shows the EDS of BiVO$_4$ and LaVO$_4$ powder respectively. Elemental analysis of the samples confirms the presence of all elements in the composition of the sample with no extra lines due to any contamination.
UV-Visible Diffuse reflectance spectra (UV-DRS) for LaVO₄ and BiVO₄ powders are shown in Figures 4.52 and 4.53 respectively. The spectra indicates the maximum absorption for LaVO₄ is in the UV region whereas for BiVO₄ the $\lambda_{\text{max}}$ lies in the visible region. Hence photocatalytic activity of LaVO₄ can only be observed for and irradiation of dye solution with electromagnetic radiation of 270-280nm. On the otherhand, BiVO₄ with its highest absorption at 400nm is clearly a visible light activated catalyst. This observation once again confirms the crystalline phase of resultant BiVO₄ is monoclinic and not tetragonal. The absorption spectra of methylene blue solution in the region 200-800 nm is shown in the Figure 4.54 which shows the $\lambda_{\text{max}}$ at 665 nm.

![Fig. 4.52 UV-Vis diffuse reflectance spectrum of LaVO₄](image)
Fig. 4.53 UV-Vis diffuse reflectance spectrum of BiVO₄

Fig. 4.54 Absorption spectrum of Methylene blue solution
Photocatalytic activity:

The photocatalytic activity of BiVO$_4$ for aqueous methylene blue was investigated under visible light irradiation of 400W halogen lamp. Methylene blue solution (5ppm in 50ml) containing 100mg of BiVO$_4$ was used and the initial pH was adjusted to 8.5. Before the solution was exposed to light for halogen lamp, the solution was stirred for 30 minutes to obtain equilibrium between the BiVO$_4$ powder and the dye solution. Then the solution was then exposed to the light from the halogen lamp and the solution was collected at time intervals of 30 minutes and was centrifuged. The supernatent solution was used to record the absorption using UV-visible spectrophotometer. The spectra in the region of 400-800nm are shown in figure 4.55. From the spectra it can be noticed that degradation of methylene blue could be observed was 30 min. Systematic studies of the effect of pH, amount of catalyst, concentration of dye are in progression.

Fig.4.55 Absorption spectra at different time intervals of methylene blue containing BiVO$_4$
4.6. CONCLUSIONS

Synthesis of AWO₄ (A = Ca, Sr, Ba, Pb and Cd) has been achieved at room temperature through SSM reaction between respective metal chlorides and sodium tungstate. XRD patterns of dried powders obtained by mixing stoichiometric quantities of the respective reactants, ground for half an hour with subsequent removal of bye product NaCl by washing indicated formation of phase pure tungstates of Ca, Sr, Ba and Pb with scheelite structure and CdWO₄ of wulframite structure. The Raman spectra and FT-IR spectra of all the samples agreed well with the literature data. From the microstructural investigation it is clear that CdWO₄ exhibited a different morphology of anisotropic particles compared to BaWO₄, CaWO₄, SrWO₄ and PbWO₄ powders which showed particles with no characteristic morphology. Particle size was estimated to be of the order of µm in all cases. Elemental analysis of the samples confirmed the presence of all elements in the composition of the sample AWO₄ with no extra lines due to any contamination.

A simple low temperature solid state metathetic synthesis has been developed for the preparation of MWO₄ (M = Fe, Mn, Co, Ni and Zn) powders using respective metal chlorides and sodium tungstate as precursors. XRD patterns of respective powders obtained by mixing stoichiometric quantities of the reactants, ground for two hours followed by heat treatment at 400°C for 4hrs, and washed free of chloride indicated formation of respective phase pure metal tungstates. Reaction temperatures reported for the synthesis of transition metal tungstates are less compared to these solid-state methods. The Raman spectra and FT-IR spectra of all the samples agreed well with the literature data. From the microstructural investigation it is clear that NiWO₄ showed a typical morphology with
formation of spherical particles when compared to MnWO₄, FeWO₄, CoWO₄ and ZnWO₄ powders which showed particles with no characteristic morphology. Particle size was estimated to be of the order of µm in all cases. Elemental analysis of the samples confirmed the presence of all elements in the composition of the sample with no extra lines due to any contamination.

Phase pure BaSnO₃ and BaZrO₃ have been synthesized successfully by solid-state metathetic reactions at temperatures lower than those reported for conventional solid-state reactions of oxide precursors. Simple precursors of BaCl₂ along with Na₂SnO₃ and K₂[ZrO(C₂O₄)₂] were made use of instead of oxides or carbonates. Optimum temperature for the formation of each compound has been reported. The Raman spectra and FT-IR spectra of all the samples are well coincides with the literature data. From the microstructural investigation it is clear that BaZrO₃ mostly contains spherical particles of nearly uniform size where as BaSnO₃ indicates particles of varying size in the µm range with no characteristic shape. Elemental analysis of the samples confirmed the presence of all elements in the composition of the sample with no extra lines due to any contamination.

Phase pure LaFeO₃ and BiFeO₃ could be obtained by heat treatment of solid mixtures of MCl₃ (M=La, Bi) and K₃[Fe(C₂O₄)₃] at different temperatures. Further LaFeO₃ were also be obtained from the heat treatment of LaCl₃ and K₃[Fe(CN)₆] solid mixture of 1:1 mole ratio at 600°C where as BiFeO₃ was not formed from the heat treatment of the stoichiometric mixture of BiCl₃ and K₃[Fe(CN)₆] even upto 800°C. Synthesis procedure reported in the thesis indicated that phase pure yielded LaFeO₃ and BiFeO₃ are obtained at considerably lower temperatures compared to corresponding solid-state syntheses making use of pure oxide precursors of La₂O₃/Bi₂O₃ and Fe₂O₃. FT-IR of
the samples agreed well with the literature. SEM micrographs of the samples showed no characteristic morphology with particle size in order of μm range. Elemental analysis of the samples confirmed the presence of all elements in the composition of the sample with no extra lines due to any contamination.

A facile room temperature solid state metathetic synthesis has been developed for the preparation of the most difficult phases of tetragonal lanthanum vanadate and monoclinic bismuth vanadate using respective metal chlorides and sodium orthovanadate as reactants. XRD patterns of dried powders obtained by grinding a mixture of stoichiometric quantities of the respective reactants for 2 hours followed by subsequent removal of bye product NaCl by washing, indicated formation of phase pure samples.

In conclusion, it may be reinstated that successful solid-state metathetic synthesis has been developed for the following technologically useful ABO₃ and ABO₄ type mixed metal oxides.

(i) MWO₄ (M=Ca, Sr, Ba, Pb and Cd)
(ii) MWO₄ (M=Mn, Fe, Co, Ni and Zn)
(iii) BaSnO₃, BaZrO₃
(iv) LaFeO₃, BiFeO₃
(v) LaVO₄, BiVO₄

The visible light photocatalytic activity of BiVO₄ towards degradation of methylene blue is also explored.