Chapter 6

Investigation of the Structural and Photocatalytic Properties of Bismuth based Mixed Metal Oxides with Scheelite Structure
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INVESTIGATION OF THE STRUCTURAL AND PHOTOCATALYTIC PROPERTIES OF BISMUTH BASED MIXED METAL OXIDES WITH SCHEELITE STRUCTURE

6.1. Introduction

The scheelite (e.g. CaWO₄) structure with ABO₄ stoichiometry (Figure 6.1) containing AO₈ polyhedra and BO₄ tetrahedra, is an important structural type. Several bismuth based mixed metal oxides were known to crystallize in this structure. Based on the choice of A and B cations, various scheelite based oxides have been identified for different applications [6.1-6.4].

Figure 6.1: Structural representation of scheelite (CaWO₄).
Especially, molybdates and tungstates possessing scheelite structure are extensively being investigated for the properties such as photoluminescence, scintillation detectors, and fibre optics and for application as photocatalysts [6.5-6.7]. For example, CdWO$_4$ synthesized via hydrothermal method showed excellent activity towards the photodegradation of aqueous Methyl Orange (MO) and Rhodamine B (Rh B) dye solutions [6.8]. Nanorods of ZnWO$_4$ showed significant influence on the photocatalytic activity for the decomposition of Rh B dye solution and for gaseous formaldehyde degradation under UV irradiation [6.9]. The photocatalytic activity of ZnWO$_4$ has been further enhanced by fluorine doping by a hydrothermal method of synthesis and the modified catalysts were used for the degradation of Rh B dye solutions under UV light irradiation [6.10]. RuO$_2$ loaded PbWO$_4$ showed high and stable photocatalytic activity for the overall splitting of water, under UV irradiation [6.11].

BiVO$_4$ is a very well known visible light based photocatalyst adopting the scheelite structure [6.12]. Bismuth vanadate can adopt various crystal structures such as tetragonal scheelite (t-s), monoclinic scheelite (m-s) and tetragonal zircon (t-z) [6.13]. Kudo et al [6.14] reported that monoclinic scheelite BiVO$_4$ is much more active than the tetragonal scheelite for O$_2$ evolution from aq. AgNO$_3$ solution under visible light. The synthesized catalysts, when evaluated for the photocatalytic activities under UV and visible light irradiation for the degradation of Rh B and MB dyes revealed the order of efficiencies to be (m-s) BiVO$_4$ > (t-z) BiVO$_4$ > (t-s) BiVO$_4$ [6.15].

The probability of the substitution of several atoms with different oxidation states in both the A and B sites of the scheelite ABO$_4$ structure have resulted in a rich family of solid solution compounds [6.16-6.17]. Moreover, the band structure can be tuned
by the appropriate solid solutions between compounds with different band gaps and currently has been regarded as one of the efficient methods for the development of new photocatalysts. Kudo et al [6.18] reported the photophysical and photocatalytic properties of molybdates with scheelite structure, such as (NaBi)MoO$_4$ ($E_g$: 3.1 eV) and (AgBi)MoO$_4$ ($E_g$: 3.0 eV) which were active for the evolution of O$_2$ from an aqueous solution containing an electron acceptor. The corresponding tungstate, (NaBi)WO$_4$ ($E_g$: 3.5 eV) produced H$_2$ from an aqueous solution containing an electron donor [6.18]. Jinhua Ye [6.19] reported new photocatalysts CaBiVMO$_8$ (M = W, Mo), based on the solid solution of BiVO$_4$ and CaMO$_4$ (M = W, Mo) and Na$_{0.5}$Bi$_{1.5}$VMoO$_8$, based on the solid solution of BiVO$_4$ and (NaBi)MoO$_4$ for the oxygen evolution from AgNO$_3$ solutions under visible light irradiation [6.20]. Nanocrystals of (AgIn)WO$_4$ have been synthesized with unique surface structures and were demonstrated as efficient photocatalysts for the decomposition of harmful organics and water splitting [6.21]. The above set of examples and their applications motivated us to study the solid solution of PbMO$_4$ (M = W, Mo) and BiVO$_4$ for their structural and photocatalytic properties.

The present chapter describes the synthesis of BiPbVMO$_8$ (M = W, Mo) by the conventional solid state method and their characterization by PXRD, UV-Visible diffuse reflectance spectroscopy and Raman spectroscopy. The samples were evaluated for the photocatalytic degradation of methylene blue (MB) dye solution under UV/visible light irradiation. Along with these, several known molybdates and tungstates such as (AgBi)WO$_4$, (AgBi)MoO$_4$, and (Pb$_{0.75}$Bi$_{0.25}$)MoO$_4$ were also synthesized and have been examined for photocatalytic activities and these results are also summarized in this chapter.
6.2. Experimental

BiPbVMO$_8$ (M = W, Mo) compounds were prepared by mixing and heating stoichiometric amounts of Bi$_2$O$_3$ (Aldrich, 99.9%), Pb(NO$_3$)$_2$ (Aldrich, 99.6%), V$_2$O$_5$ (Aldrich, 99.5%) and WO$_3$ (Thomas Baker, 99.9%) or MoO$_3$ (Aldrich, 99.9%) initially at 600 °C for 12 h, reground and further calcined at 800 °C for 12 h and quenched in air. Similarly, (AgBi)WO$_4$, (AgBi)MoO$_4$ and (Pb$_{0.75}$Bi$_{0.25}$)MoO$_4$ compositions were also synthesized using the stoichiometric amounts of AgNO$_3$ (Rankem, 99.5%), Bi$_2$O$_3$, WO$_3$, MoO$_3$, Pb(NO$_3$)$_2$, Na$_2$CO$_3$ and dried La$_2$O$_3$ (Aldrich, 99.9%) under similar heating conditions with intermediate grindings for the phase formation.

6.3. Results and discussion

The phase purity of the oxides (BiPb)(VM)O$_4$ (M = W, Mo) were confirmed by the PXRD patterns of the synthesized compounds (Figure 6.2). The diffraction peaks could be very well indexed in a tetragonal lattice (S.G.: $I4_1/a$). The Rietveld refinement of the monophasic samples were performed over a range of 15° ≤ 2θ ≤ 90° using TOPAS program [6.22, 6.23] with pseudo-Voigt as the peak shape. The refinement was based on the method of least squares with six background coefficients of a polynomial function. The obtained lattice parameters were $a = 5.2865(3)$, $c = 11.8958(3)$ Å for (BiPb)(VW)O$_4$; and $a = 5.2793(2)$, $c = 11.9387(1)$ Å for (BiPb)(VMo)O$_4$. The best fit resulted in the reliability factors $R_I = 6.838$ % and 5.871 %; and Gof = 2.5305 and 2.194 for (BiPb)(VM)O$_4$ (M = W, Mo) respectively. The positional parameters from the refinement are listed under Table 6.1 and the profile fitting has been shown in the Figure 6.3 (a) and (b). The structure with the mixed occupancy of 0.5Bi and 0.5Pb along with that of (V$_{0.5}$W$_{0.5}$)O$_4$ or (V$_{0.5}$Mo$_{0.5}$)O$_4$ indeed
confirmed the solid solution formation from the end members BiVO₄ and PbMO₄ (M = W, Mo), respectively.

Figure 6.2: PXRD patterns of (BiPb)(VM)O₄ (M = W, Mo) crystallizing in tetragonal symmetry (S.G.: I4₁/a).

Table 6.1: Positional parameters of (BiPb)(VM)O₄ (M = W, Mo) obtained from the Rietveld [6.22] refinement of the powder samples.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uiso(Å²)</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>0</td>
<td>0.25</td>
<td>0.625</td>
<td>0.025</td>
<td>0.50</td>
</tr>
<tr>
<td>Pb</td>
<td>0</td>
<td>0.25</td>
<td>0.625</td>
<td>0.025</td>
<td>0.50</td>
</tr>
<tr>
<td>V</td>
<td>0</td>
<td>0.25</td>
<td>0.125</td>
<td>0.025</td>
<td>0.50</td>
</tr>
<tr>
<td>W/Mo</td>
<td>0</td>
<td>0.25</td>
<td>0.125</td>
<td>0.025</td>
<td>0.50</td>
</tr>
<tr>
<td>O (M = W)</td>
<td>0.1695(2)</td>
<td>0.4625(3)</td>
<td>0.2138(1)</td>
<td>0.025</td>
<td>1.00</td>
</tr>
<tr>
<td>O (M = Mo)</td>
<td>0.1327(1)</td>
<td>0.4964(2)</td>
<td>0.1883(1)</td>
<td>0.025</td>
<td>1.00</td>
</tr>
</tbody>
</table>
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Figure 6.3: Rietveld refinement of (a) (BiPb)(VW)O$_4$ and (b) (BiPb)(VMo)O$_4$ (Observed, calculated and difference patterns are given by blue, red and grey lines, respectively; Bragg positions are given by grey/blue vertical lines).

The presence of both VO$_4$ and (W/Mo)O$_4$ tetrahedral groups was also confirmed by the Raman spectra of the synthesized compounds (Figure 6.4). The factor group analysis and the assignment of the Raman bands were carried out. The (Mo/V/W)O$_4$ tetrahedrons possessing a cubic point group symmetry $T_d$ were characterized by four Raman active internal vibrations, viz. $v_1$ ($A_I$) symmetric stretching mode, $v_2$ ($E$) doubly degenerate symmetric bending mode, $v_3$ ($T_2$) triply degenerate antisymmetric stretching mode and, $v_4$ ($T_2$) triply degenerate antisymmetric bending mode [6.24]. The bands at
818 and 821 cm\(^{-1}\) in the Raman spectra of (BiPb)(VW)O\(_4\) and (BiPb)(VMo)O\(_4\) correspond to V-O symmetric stretching mode (Figure 6.4 (a) and (b)) \[6.25\]. Also, the symmetric stretching modes, \(v_1\) for the W-O and Mo-O were observed at 908 and 878 cm\(^{-1}\) respectively, matching well with the literature \[6.26\]. The antisymmetric stretching \((v_3)\) was observed to merge within the symmetric Raman bands in the range of 700 - 850 cm\(^{-1}\). In addition, the Raman bands observed in the range of 300 - 425 cm\(^{-1}\) were attributed to the bending modes \((v_2\) and \(v_4)\) for (Mo/V/W)O\(_4\) tetrahedra \[6.27\].

![Raman spectra of (BiPb)(VW)O\(_4\) and (BiPb)(VMo)O\(_4\).](image)

**Figure 6.4:** Raman spectra of (a) (BiPb)(VW)O\(_4\), and (b) (BiPb)(VMo)O\(_4\).

Figure 6.5 shows the PXRD patterns of some of the known bismuth containing scheelite compounds, such as (AgBi)WO\(_4\), (AgBi)MoO\(_4\) and (Pb\(_{0.75}\)Bi\(_{0.25}\))MoO\(_4\). Here again, the PXRD patterns could be very well indexed in the tetragonal symmetry with
the space group $I4_1/a$. The refined lattice parameters of all these compounds are summarized in Table 6.2.

![PXRD patterns](image)

**Figure 6.5:** PXRD patterns of (a) (AgBi)WO$_4$, (b) (AgBi)MoO$_4$ and (Pb$_{0.75}$Bi$_{0.25}$)MoO$_4$ crystallizing in tetragonal symmetry adopting scheelite structure.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$ [Å]</th>
<th>$c$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(AgBi)WO$_4$</td>
<td>5.3078(3)</td>
<td>11.6204(7)</td>
</tr>
<tr>
<td>(AgBi)MoO$_4$</td>
<td>5.2923(5)</td>
<td>11.6551(1)</td>
</tr>
<tr>
<td>(Pb$<em>{0.75}$Bi$</em>{0.25}$)MoO$_4$</td>
<td>5.3975(2)</td>
<td>12.0035(2)</td>
</tr>
</tbody>
</table>

**Table 6.2:** Lattice parameters of (AgBi)XO$_4$ (X = W, Mo) obtained by the Le Bail [6.28] fitting using TOPAS software [6.23].

Figure 6.6 shows the UV-Visible diffuse reflectance spectra of the synthesized bismuth based scheelite compounds. A visible absorption is expected out of the bismuth based
oxides, especially because of the possible transition involving the valence band comprising of O 2\( p \) and Bi 6\( s \) orbitals, to that of the conduction band constituted from the transition metal based \( d \) orbitals [6.29]. In the present case, (BiPb)(VW)O\(_4\) and (BiPb)(VMo)O\(_4\) oxides showed clear visible light absorptions with \( \sim 522 \) and \( \sim 533 \) nm as the absorption edges, while (AgBi)MoO\(_4\) showed a clear visible light absorption around \( \sim 425 \) nm, (AgBi)WO\(_4\) absorbed around \( \sim 390 \) nm. The estimated band gaps, from the diffuse reflectance spectra, were 2.36, 2.29, 3.11, 2.92 and 2.84 eV, for (BiPb)(VX)O\(_4\), (AgBi)XO\(_4\) for X = W, Mo and (Pb\(_{0.75}\)Bi\(_{0.25}\))MoO\(_4\) respectively. The sharp absorption spectra of these compounds suggested them to be potential photocatalysts, and thus the synthesized compounds were tested for the photocatalytic degradation of dyes, such as Methylene Blue (MB), under light irradiation.

![Figure 6.6](image)

**Figure 6.6:** Diffuse reflectance spectra of the scheelite phases, (a) plot of wavelength versus absorbance, and (b) plot of \( h\nu \) versus Kubelka Munk function \((a\nu)^{1/2}\) for the estimation of band gap (in eV).

Figure 6.7 shows the decrease in concentration of MB dye solution in the presence of the scheelite based compounds synthesized in the present study over a period of light irradiation. The degradation curves revealed a moderate photocatalytic response over these catalysts for MB dye under 125 W UV-Visible light irradiation at pH 10. The
results also indicated that (BiPb)(VW)O$_4$ and (BiPb)(VMo)O$_4$ showed comparatively higher rate of degradation than the silver containing samples (AgBi)XO$_4$ ($X = W, Mo$).

![Figure 6.7: Photocatalytic degradation of MB dye under 125 W UV-Visible light irradiation at pH 10 over scheelite based compounds.](image)

6.4. Conclusion

The composition and the tetragonal symmetry (S.G.: $I4_1/a$) of the new oxides (BiPb)(VW)O$_4$ and (BiPb)(VMo)O$_4$ members of the solid solution between the two scheelite based oxides BiVO$_4$ and PbMO$_4$ ($M = W, Mo$), were confirmed by the Rietveld refinement of the PXRD patterns of these oxides. The presence of both VO$_4$ and (W/Mo)O$_4$ tetrahedral groups was also analyzed by the Raman spectroscopy. These compounds along with bismuth based molybdates and tungstates, such as (AgBi)WO$_4$, (AgBi)MoO$_4$, and (Pb$_{0.75}$Bi$_{0.25}$)MoO$_4$ showed a sharp visible light absorption in the UV-Visible diffuse reflectance spectra. The phase pure samples showed adequate photocatalytic degradation of the common dye pollutant methylene blue (MB) under UV-Visible light irradiation.


References


