Chapter 6

Electrical conductivity and phase transition studies in Mn-doped Bi$_4$V$_2$O$_{11-\delta}$ oxide-ion conductor.
6.1. Introduction

Oxide-ion conduction in ceramics was evidenced on calcium stabilized zirconia by Nernst in 1905. A century later, stabilized zirconia remains the reference electrolyte for most applications of solid oxide electrolytes such as solid oxide Fuel Cells, oxygen pumps and ceramic oxygen generators [1-10]. However, its electrical properties are mediocre and require working at elevated temperature, (800–1200°C) [11-15]. In order to decrease these operating temperatures, other classes of bismuth-based electrolyte materials were investigated. Among these, the BIMEVOX compounds are considered as the best oxide-ion conductors at moderate temperatures, 400–600°C [16-18]. These phases are generally formulated as \((\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}\) where \(n\) varies from 1 to 8 [19-25]. Solid solutions based on bismuth vanadate, \(\text{Bi}_4\text{V}_2\text{O}_{11-\delta}\), the first member of perovskite Aurivillius homologous series with \(n=1\), have been studied extensively as most promising basic compounds for ionic conductors [26-28]. \(\text{Bi}_4\text{V}_2\text{O}_{11-\delta}\) undergo two types of reversible phase transitions viz \(\alpha \leftrightarrow \beta\) and \(\beta \leftrightarrow \gamma\) close to 700 and 850K respectively [24, 29-32]. Many reports have established the fact that the tetragonal \(\gamma\)-form can be stabilized at room-temperature by suitable metal ion doping at the vanadium site [26, 33-37]. Incorporation of vacancies in the vanadate layer may stimulate a decrease in coordination
number of vanadium cations from 6 to 4 or 5 that influences the stability limits and properties of the BIMEVOX polymorph modifications [38]. Many cationic substitutions have been successfully attempted [26, 35, 36, 39-41] in order to stabilize the high temperature γ-form down to room temperature.

The present chapter deals with the synthesis, characterization and oxide-ion conductivity of BIMNVOX system, a new member of BIMEVOX family.

6.2. Experimental

\[ \text{Bi}_4\text{Mn}_x\text{V}_{2-x}\text{O}_{11-(x/2)-\delta} \text{ samples in the composition range } 0.07 \leq x \leq 0.30 \]

were prepared by conventional solid state reactions from stoichiometric mixtures of Bi\(_2\)O\(_3\), V\(_2\)O\(_5\) and MnO\(_2\) according to the substitution equation:

\[ 2\text{Bi}_2\text{O}_3 + x \text{MnO}_2 + (1-x/2) \text{V}_2\text{O}_5 \rightarrow \text{Bi}_4\text{Mn}_x\text{V}_{2-x}\text{O}_{11-(x/2)-\delta} \quad (6.1) \]

The reactants were thoroughly mixed in an agate mortar with acetone and toluene (1:1) solvent for ~30 minutes. The resulting pastes were then transferred into nickel crucibles and heated in a muffle furnace at 740°C for 24 hours with intermittent cooling, grinding and mixing with acetone–toluene solvent. The finely grounded powders were hydraulically pressed into pellets of dimensions 2.4cm diameter and 0.1cm thickness by applying isostatic pressure of 980 MPa using Spectralab SL–98 and were then sintered for 12 hours and gradually cooled in air to room temperature. The
X–ray diffraction data of these prepared samples was recorded on a Rigaku/Max–B X–ray diffractometer using Ni–filtered CuKα radiation (λ = 1.54060 Å) with diffraction angle range 5° ≤ 2θ ≤ 90° and an increment of 0.05° at scan time of 0.6 second/increment. The refinement of the unit cell parameters was done by powder X program.

The FT–IR spectra were recorded in transmittance mode on a Perkin–Elmer 1 spectrophotometer by diluting the sample with 10% w/w KBr of analytical grade. The spectra were scanned in the region of 4000–400cm⁻¹.

Moreover differential thermal analysis measurements were recorded on a Schimatzu DTA–60 thermal analyzer by taking ~15mg of dry sample in a current flow of N₂ (15ml/min) by maintaining the heating rate at 10°C/min from ambient to 800°C.

The AC impedance measurements were recorded on Solarton 1620 analyzer in the frequency range of 5 – 6.5×10⁶ Hz with input AC signal ~50mV. The electrical conductivity was measured in the temperature range of 200–800°C over two cycles of heating and cooling with a step of 20°C. The heating rate was maintained at 1°C/min with 15min stabilization time in each step. The pellet faces were made conducting by placing between two identical silver electrodes.
6.3. Results and discussion

6.3.1. FT-IR Spectroscopy

The FT-IR spectra of Bi₄MnxV₂₋ₓO₁₁₋(ₓ/₂)₋δ solid solutions is shown in Fig. 6.1. It is clearly noticed that with increase in Mn concentration, the vibration position of vanadate tetrahedra shifts to lower frequencies for e.g. the shift from 1011 cm⁻¹ for x=0.10 to 966 cm⁻¹ for x=0.30. This shift in vanadate tetrahedra is due to the substitution of Mn⁴⁺ for V⁵⁺. However, the position of Bi-O bands (439-417 cm⁻¹) does not change much for all compositions. The disappearance of fine structures for x ≥ 0.20 in the vanadate anion region shows the presence of crystallographic disordering in the structure of perovskite layers in the tetragonal phase [42-44]. According to XRD analysis (discussed in next section) the disappearance of fine structures in the spectra for x ≥ 0.20 can be attributed to the phase transition to γ-polymorph which arises due to the increased distortion in the vanadate tetrahedra [45].

The various IR bands for composition 0.10 ≤ x ≤ 0.30 are listed in Table 6.1. For x ≤ 0.17, the IR spectrum seems to mimic the parent compound, which shows symmetric νₛ(V–O) stretching, asymmetric νₘₙ(V–O) stretching and asymmetric deformation [δₘₙ(O–V–O)] modes of vibration assigned to vanadate anion in α–Bi₄V₂O₁₁₋δ [46].
Fig. 6.1: FT-IR pattern for the system Bi$_4$Mn$_x$V$_{2-x}$O$_{11-(x/2)-\delta}$ in the composition range 0.07 $\leq$ x $\leq$ 0.30.
Table 6.1: FT-IR data of the Bi$_4$Mn$_x$V$_{2-x}$O$_{11-(x/2)-\delta}$ for $0.10 \leq x \leq 0.30$.

<table>
<thead>
<tr>
<th>x</th>
<th>$\nu_s$(V-O), cm$^{-1}$</th>
<th>$\nu_{as}$(V-O), cm$^{-1}$</th>
<th>$\delta_{as}$(O-V-O), cm$^{-1}$</th>
<th>$\nu$(Bi-O), cm$^{-1}$</th>
<th>$\nu$(Mn-O), cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>747</td>
<td>1011, 981,</td>
<td>666, 630,</td>
<td>439</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>882, 822</td>
<td></td>
<td></td>
<td>553</td>
</tr>
<tr>
<td>0.13</td>
<td>741</td>
<td>991, 958,</td>
<td>651, 619,</td>
<td>432</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>872</td>
<td></td>
<td></td>
<td>538</td>
</tr>
<tr>
<td>0.17</td>
<td>736</td>
<td>983, 953,</td>
<td>644, 518,</td>
<td>424</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>864</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>732</td>
<td>975, 937,</td>
<td>630, 505,</td>
<td>416</td>
<td>567</td>
</tr>
<tr>
<td></td>
<td></td>
<td>844</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.30</td>
<td>724</td>
<td>966, 817,</td>
<td>624, 506,</td>
<td>417</td>
<td>565</td>
</tr>
</tbody>
</table>
Apart from all these normal modes of vibration, additional band observed nearly at 417-439 cm$^{-1}$ can be properly assigned to the stretching mode of Bi-O bond vibration in the bismuthate layer [47, 48].

6.3.2. X-ray powder diffraction analysis

Fig. 6.2 illustrates the room temperature XRD patterns of BIMNVOX system in the composition range $0.07 \leq x \leq 0.30$. For the sake of visibility of the important sublattice peak convergence, which shows the variation in the phase structures as a function of composition, the diffraction data have been graphed in the 2θ range 20-60°. For compositions with $x \leq 0.17$, the singlet indexed 220 ca. $2\theta \approx 46.17°$, shows the existence of orthorhombic $\beta$-phase of higher symmetry having space group $ABa2$. However for $x=0.20$ and $x=0.30$, the tetragonal $\gamma$-phase is stabilized as evidenced by the convergence of the sublattice doublet ca. $2\theta \approx 32.5°$, indexed as (202, 200) into a singlet indexed in tetragonal cell as (110) [48, 49-51].

The variation in the unit cell parameters (a, b and c) and volume (V) as a function of composition $x$ is depicted in Fig. 6.3. Two line regions can be visualized associated with $\beta \leftrightarrow \gamma$ phase transitions. It is interesting to note that the system with composition $x=0.07$ can be considered as lower limit of $\beta$–phase stability having mean cell ($a \approx 5.522$ Å, $b \approx 5.613$ Å, $c \approx 15.231$ Å).
Fig. 6.2: X-ray diffraction patterns for Bi$_4$Mn$_x$V$_{2-x}$O$_{11-(x/2)-\delta}$

$(0.07 \leq x \leq 0.30)$ samples.
Fig. 6.3: Variation in the unit cell parameters and cell volume of BIMNVOX system as a function of composition (x).
Table 6.2: Unit cell parameters for various compositions of the system $\text{Bi}_4\text{Mn}_x\text{V}_{2-x}\text{O}_{11-(x/2)-\delta}$.
and mean volume \((V = 472.085 \, \text{Å}^3)\) with respect to the \(\beta\)-phase model with space group \(\text{Aba2}\).

Table 6.2 lists the results of refined unit cell parameters in BIMNVOX system. The system with composition \(x = 0.20\) can be considered as the transition composition to the tetragonal \(\gamma\)-phase with unit cell parameters \((a \approx 3.925 \, \text{Å}, c \approx 15.303 \, \text{Å})\) and mean volume \((V = 471.362 \, \text{Å}^3)\). It is also noticed that \(c\) parameter increases with increase in Mn concentration, this can be attributed to the substitution of smaller \(V^{5+}\) (0.59 Å) by larger \(\text{Mn}^{4+}\) (0.72 Å) [52] in 6–fold co–ordination geometry. Such behavior for BIMNVOX is generally typical for other BIMEVOXes which have been reported earlier [51, 53–56].

### 6.3.3. Differential thermal analysis

The DTA thermograms of BIMNVOX system as a function of composition is represented in Fig. 6.4. For composition \(x \leq 0.17\), the
endothermic peaks observed in the temperature range 361-399°C, reveal the presence of $\beta \leftrightarrow \gamma$ phase transition. However, for $x = 0.20$ and $x = 0.30$, the endothermic peaks at 520 and 498°C respectively could be correlated with subtle incommensurate disordering of the oxide-ion vacancies in the perovskite layer associated with $\gamma' \leftrightarrow \gamma$ phase transition.
Fig. 6.4: DTA thermograms of BIMNVOX system versus composition (x).
Table 6.3: Transition temperatures and enthalpies determined from DTA thermo grams for the system

\[ \text{Bi}_4\text{Mn}_x\text{V}_{2-x}\text{O}_{11-(x/2)-\delta}. \]

<table>
<thead>
<tr>
<th>x</th>
<th>( \beta \leftrightarrow \gamma )</th>
<th>( \gamma' \leftrightarrow \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C)</td>
<td>( \Delta H ) (J.g(^{-1}))</td>
</tr>
<tr>
<td>0.07</td>
<td>399</td>
<td>24.06</td>
</tr>
<tr>
<td>0.13</td>
<td>361</td>
<td>22.18</td>
</tr>
<tr>
<td>0.17</td>
<td>383</td>
<td>17.60</td>
</tr>
<tr>
<td>0.20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.30</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The values of transition temperatures and corresponding enthalpies are listed in Table 6.3. It is noticed that enthalpy (ΔH) decreases on increasing the dopant concentration which is also evident for other BIMEVOXes [57, 58].

6.3.4. AC impedance spectroscopy

The equivalent circuit representation of electrolyte is composed of capacitances (C), inductances (L), resistances (R) and constant phase elements (CPE). The impedance of a CPE can be calculated by using equation, (6.2)

\[ Z(\omega) = \frac{1}{B(j\omega)^n} ; j = \sqrt{-1} \]  

(6.2)

where \( \omega \) is the angular frequency of the applied electric field, and the coefficient B and exponent n (-1 < n < 1) are the two specific parameters of CPE. The capacitances (\( C_g \) and \( C_{gb} \)) and the relaxation time (\( \tau_g \) and \( \tau_{gb} \)) at the grain boundary can be obtained by the equations, (6.3) and (6.4)

\[ C_i = \frac{1}{R_i \omega_i} \]  

(6.3)

\[ \tau_i = \frac{1}{\omega_i} = C_i R_i \]  

(6.4)

The total resistances (\( R_t \)) can be calculated from the values of grain (\( R_g \)) and grain boundary (\( R_{gb} \)) resistances as follows:

\[ R_t = R_g + R_{gb} \]  

(6.5)
R_g and R_gb can be exactly calculated from the intercept of the corresponding Z’–axis. The values of angular frequencies at grain (ω_g) and grain boundary (ω_gb) are calculated from the frequency of the applied field at which the imaginary part of the impedance Z'' reaches a maximum according to equation (6.6):

$$\omega_i = 2\pi f_{\text{max},i}$$  \hspace{1cm} (6.6)

where \(f_{\text{max},i}\) is the frequency at maxima of the grain (i \(\equiv\) g) and at the grain boundary (i \(\equiv\) gb) semicircles respectively [59].

Complex impedance spectra of Bi_{4}\text{Mn}_x\text{V}_{2-x}\text{O}_{11-(x/2)-\delta} solid solutions for six different compositions at 220°C are shown in Fig. 6.5. It is clearly seen from the figure that the inclined spike is absent for the lower composition x=0.07. This is due to the limited frequency range (5 – 6.5\times10^6 Hz) of the impedance measurement. This reflects the high ferroelectric behavior of the sample at this value of cationic substitution. This is the typical behavior of other \(\alpha\)-BIMEVOXes also [60, 61]. For composition 0.10 \(\leq\) x \(\leq\) 0.30, the impedance plane plots show two capacitive semi circles with an inclined spike. The higher frequency semicircle corresponds to the grain contribution to oxide-ion conductivity whereas, the lower frequency semi circle is related to the grain boundary contribution to oxygen-ionic conductivity. The curved inclined spike observed in the far low frequency region is associated with
Fig. 6.5: AC impedance plane plots of BIMNVOX system for composition $0.07 \leq x \leq 0.30$ at 220 °C.
the impedance of interface between the silver electrodes and oxide-ion electrolyte [60, 62].

The values of equivalent circuit parameters estimated from the impedance plane plots are listed in Table 6.4. It can be clearly observed that for all the compositions at a constant temperature (220 °C), the values of grain resistance $R_g$ are much higher than grain boundary resistance $R_{gb}$, suggesting the greater contribution of grain to the ionic conductivity than grain boundary. It is also noticed that with increasing composition, the values of $R_g$ drops sharply up to $x=0.17$ and then it increases. The similar variation is also exhibited by $R_{gb}$, showing the role of dopant concentration on specific electrical properties of BIMNVOX system. The highest values of capacitances $C_g$ ($2.584 \times 10^{-12}$) and $C_{gb}$ ($1.661 \times 10^{-10}$) are found to be for $x=0.17$, indicating the increased permittivity of the samples associated with charge accumulation at the grain boundaries [62]. This is also further confirmed by the lowest values of the corresponding relaxation time $\tau_g$ and $\tau_{gb}$.

**6.3.5. Temperature dependence of conductivity**

Fig. 6.6 represents the Arrhenius plots of conductivities for BIMNVOX system. For composition $0.07 \leq x \leq 0.13$, two domains with
Table 6.4: AC impedance plane plots of BIMNVOX system for composition $0.07 \leq x \leq 0.30$ at 220 °C.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$R_g$(kΩ)</th>
<th>$C_g$(F)</th>
<th>$\tau_g$(s)</th>
<th>$R_{gb}$(kΩ)</th>
<th>$C_{gb}$(F)</th>
<th>$\tau_{gb}$(s)</th>
<th>$R_l$(kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.07</td>
<td>7519.279</td>
<td>$4.23\times10^{-13}$</td>
<td>$3.181\times10^{-6}$</td>
<td>5445.887</td>
<td>-</td>
<td>-</td>
<td>12965.17</td>
</tr>
<tr>
<td>0.10</td>
<td>3508.645</td>
<td>$8.483\times10^{-13}$</td>
<td>$2.976\times10^{-6}$</td>
<td>1445.888</td>
<td>$2.059\times10^{-12}$</td>
<td>$1.509\times10^{-4}$</td>
<td>4954.53</td>
</tr>
<tr>
<td>0.13</td>
<td>959.749</td>
<td>$2.580\times10^{-12}$</td>
<td>$2.476\times10^{-6}$</td>
<td>482.71</td>
<td>$1.567\times10^{-10}$</td>
<td>$7.565\times10^{-5}$</td>
<td>1442.46</td>
</tr>
<tr>
<td>0.17</td>
<td>724.109</td>
<td>$2.584\times10^{-12}$</td>
<td>$1.871\times10^{-6}$</td>
<td>333.406</td>
<td>$1.661\times10^{-10}$</td>
<td>$5.539\times10^{-5}$</td>
<td>1057.52</td>
</tr>
<tr>
<td>0.20</td>
<td>1825.455</td>
<td>$1.118\times10^{-12}$</td>
<td>$2.040\times10^{-6}$</td>
<td>792.727</td>
<td>$2.575\times10^{-12}$</td>
<td>$7.22\times10^{-5}$</td>
<td>2618.18</td>
</tr>
<tr>
<td>0.30</td>
<td>5080.52</td>
<td>$4.632\times10^{-13}$</td>
<td>$2.216\times10^{-6}$</td>
<td>2266.75</td>
<td>$9.776\times10^{-13}$</td>
<td>$8.607\times10^{-5}$</td>
<td>7347.27</td>
</tr>
</tbody>
</table>
different slopes are observed which ascribe to the presence of $\beta \leftrightarrow \gamma$ phase transition. For $x \geq 0.20$ single domains with no significant discontinuity in low and high temperature region signifies $\gamma' \leftrightarrow \gamma$ phase transition.

Fig. 6.7 shows the hysteresis loop during heating-cooling run for $x=0.17$. The presence of only two line regions of different activation energies in the Arrhenius plot and the appearance of the thermal hysteresis loop at the discontinuity during the cooling run can be attributed to the stability of $\beta$ and $\gamma$-polymorphs. It can also be noted that the high temperature region represents the fully disordered $\gamma$-phase, whereas the low-temperature region is associated with subtle incommensurate ordering of oxide ion vacancies. The above results were also previously confirmed by XRD and DTA analysis.

The low and high temperature activation energies $\Delta E_{(LT)}$ and $\Delta E_{(HT)}$ in the temperature regions (200–400°C) and (500–800°C) respectively for compositions $0.07 \leq x \leq 0.30$ were calculated by using linear square fitting to Arrhenius dependence.

$$\sigma T = D \exp\left(\frac{-E_\sigma}{kT}\right)$$

(6.7)
Fig. 6.6: Arrhenius plots of conductivity on heating for Bi$_4$Mn$_x$V$_{2-x}$O$_{11-\frac{x}{2}-\delta}$ samples.

(0.07 ≤ x ≤ 0.30)
$\log_{10}(\sigma T) = \frac{1000}{T} (K^{-1})$

Fig. 6.7: Arrhenius plots of conductivity on heating and cooling run for $x=0.17$. 
The composition dependence of low temperature conductivity ($\sigma_{300}$) is presented in Fig. 6.8. It is clearly seen that the low temperature conductivity initially increases as a function of composition up to $x = 0.17$, where it attains a maximum conductivity of $2.467 \times 10^{-5}$ S.cm$^{-1}$. After this it shows decay, particularly in the composition region of $\gamma$-phase stability. It should be noted that the otherwise maximum in $\Delta E_{(LT)}$ for $x=0.13$, corresponding to relative high conductivity, is attributed to some extent of vacancy ordering. However, the lowering in the conductivity beyond $x = 0.17$ suggests that some of the vacancy ordering energy is employed by the defect trapping effects, which have negative contribution to overall conductivity, such as the formation of defect pairs ($\text{Mn}^{4+}$ and $\text{V}^{\text{••}}_\text{O}$) [63-65].

The composition dependence of high temperature conductivity ($\sigma_{600}$) and its corresponding activation energy is depicted in Fig. 6.9. It can be noticed that the highest value of conductivity $\sigma_{600} = 0.037$ S.cm$^{-1}$ is observed for $x = 0.10$. Thereafter, the conductivity decays slowly which is also observed in other BIMEVOXes [44, 45]. It can be noticed that there are some increased values of $\Delta E_{(HT)}$ e.g. at $x=0.10$ and $x=0.17$, which are associated with vacancy ordering phenomenon in the equatorial plane of the perovskite like slabs at higher temperatures.
Fig. 6.8: Variation in the low temperature conductivity and activation energy as a function of composition (x).
Fig. 6.9: Variation in the high temperature conductivity and activation energy as a function of composition (x).
6.4. Conclusions

Substitution of V by Mn$^{4+}$ leads to the formation of a new member of BIMEVOX family formulated as Bi$_{4}$Mn$_{x}$V$_{2-x}$O$_{11-(x/2)-\delta}$. In this system β and γ-polymorphs are stabilized depending on Bi:V ratio and dopant concentration. The highest conductivity (2.467×10$^{-5}$ S.cm$^{-1}$) is obtained for $x=0.17$, where β polymorph is stabilized. Mainly the oxide ion vacancies are responsible for this high conductivity. These vacancies are disordered for fast ionic conduction.