Chapter 4

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

After the discovery of Bi$_4$V$_2$O$_{11-\delta}$ as a solid electrolyte having high ionic conductivity $\sim 0.02$ S.cm$^{-1}$ at moderate temperatures [1–10], extensive research have been carried out to obtain highest ionic conductivity at the lowest possible temperature by modifying the composition and crystal structure. Partial substitution of vanadium with metal element (e.g. Cu, Ni, Ca, Sn, Co etc) in Bi$_4$V$_2$O$_{11-\delta}$ leads to the stabilization of high temperature $\gamma$–phase to lower temperatures [2, 11–15]. Substitution of V by divalent cations results in an increase in vacancy concentration in the vanadate layer by lowering the coordination number of vanadium cations to four or five. The properties and stabilization of the polymorphs of these solid solutions significantly depend on the synthesis conditions, charge, amount and the coordination number, oxygen vacancy concentration and also on the ionic potential of the cation introduced [16, 17].

In this chapter we report a detailed study on the phase transition and ionic conductivity of the BIBAVOX system.

4.2. Experimental

Solid solutions of general formula Bi$_4$Ba$_x$V$_{2-x}$O$_{11-(3x/2)-\delta}$ in the composition range $0.07 \leq x \leq 0.30$ were prepared by conventional solid state techniques. Approximate amounts of Bi$_2$O$_3$, BaO and V$_2$O$_5$ were grounded
together for ~30 minutes in an agate mortar using 1:1 acetone–toluene solvent. The dried powders were heated in a muffle furnace for 24 hours at 740°C with intermittent cooling, grinding and mixing with acetone–toluene solvent. After cooling the grounded powders were pelletized by using the hydraulic press Spectra lab SL–98 under isostatic pressure of 980 MPa followed by sintering in air.

The FT–IR spectra of the prepared samples were collected on a Perkin Elmer 1 spectrophotometer by diluting the sample powders to exactly 10% w/w by analytical grade KBr in the wave number region of 4000-400 cm⁻¹.

The phase composition and crystal lattice parameters for various compositions were studied by X-ray powder diffraction analysis carried out on a Rigaku/Max-B diffractometer equipped with Ni-filtered radiation (λ = 1.54060 Å) with diffraction angle range 5° ≤ 2θ ≤ 90° with steps of 0.05° and scan time of 0.6 seconds per step. The sample powder was held on a SiO₂ strip arranged in θ/2θ geometry and the refinement of the unit cell parameters was done by powder X program.

The structural phase transitions in the prepared samples were studied by differential thermal analysis (DTA) measurements carried out on a Schimatzu DTA–60 thermal analyzer by taking ~15 mg dry sample in an
alumina cell in N$_2$ environment. The flow rate of N$_2$ was maintained at 30 ml/min with heating rate of 10°C per minute from ambient to 1000°C.

The electrical conductivity and AC impedance measurements were recorded on a Solartron 1620 impedance analyzer in the frequency range of 5–6.5×10$^6$ HZ with input AC signal of approximately 50 mV. Whereas the electrical conductivity measurements were taken in the temperature range of 200-800°C with a step of 20°C over two cycles of heating and cooling. In each step, the heating rate was maintained at 1°C per minute with a stabilization time of 15 minutes. The pellets were sandwiched between two identical silver electrodes in order to make them conducting.

4.3. Results and discussion

4.3.1. FT-IR Spectroscopy

Fig. 4.1 illustrates the FT-IR spectra of Bi$_4$Ba$_x$V$_{2-x}$O$_{11-(3x/2)-\delta}$ solid solutions. It is observed that for compositions 0.07 ≤ x ≤ 0.13 the IR spectrum seems to mimic the parent compound α-Bi$_4$V$_2$O$_{11-\delta}$ as reported in literature [18–20]. The bands seen in the frequency region of 525-990 cm$^{-1}$ are assigned to the vibration of VO$_4$ tetrahedra, and the fine structure seen in these bands can be attributed to the symmetric stretching and bending modes of VO$_4$ tetrahedra, which arises due to the variation in the (V–O) bond length in the range of 1084-1079Å [5, 19].
Fig. 4.1: FT–IR pattern for the system Bi$_x$Ba$_{1-x}$V$_{2-x}$O$_{11-(3x/2)-δ}$ in the composition range $0.07 \leq x \leq 0.30$. 
Table 4.1: FT-IR data of the Bi$_x$Ba$_x$V$_{2-x}$O$_{11-(3x/2)-\delta}$ for $0.07 \leq x \leq 0.30$.

<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>$\nu$(Ba-O), cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.07</td>
<td>743</td>
<td>996, 967, 881, 822</td>
<td>662, 622, 550, 523</td>
<td>451</td>
<td>579</td>
</tr>
<tr>
<td>0.13</td>
<td>735</td>
<td>989, 961, 873, 813</td>
<td>658, 617, 543</td>
<td>443</td>
<td>581</td>
</tr>
<tr>
<td>0.17</td>
<td>728</td>
<td>981, 949, 861</td>
<td>651, 609, 543</td>
<td>433</td>
<td>573</td>
</tr>
<tr>
<td>0.20</td>
<td>720</td>
<td>976, 848</td>
<td>642, 538, 543</td>
<td>430</td>
<td>564</td>
</tr>
<tr>
<td>0.30</td>
<td>716</td>
<td>970, 837</td>
<td>632, 529, 424</td>
<td>558</td>
<td></td>
</tr>
</tbody>
</table>
The absorption band observed in the range of 424-451 cm\(^{-1}\) could be properly assigned to stretching vibration of Bi–O bond [21, 22].

Table 4.1 lists the values of important IR bands for BIBAVOX system vs. composition. The bands observed in the frequency region of 558-579 cm\(^{-1}\) for composition 0.07 ≤ x ≤ 0.30 are probably assigned to the stretching vibration of Ba–O bond. The shift of \(\nu_s(V\text{-O})\) and \(\nu_{as}(V\text{-O})\) to lower frequencies and the disappearance of fine structure in the VO\(_4\) vibration region (525-990 cm\(^{-1}\)) can be attributed to the distortion in the vanadate anion structure resulting from increased barium concentration [23-25].

### 4.3.2. X-ray powder diffraction analysis

The phase composition and the crystal lattice parameters were studied by X-ray powder diffraction analysis. Fig. 4.2 shows the diffraction pattern of the prepared samples in the composition range 0.07 ≤ x ≤ 0.30. The diffraction data have been graphed in the 2\(\theta\) range 20–60° for the sake of visibility of the important sublattice peak convergence. It is noticed that for x ≤ 0.13 \(\alpha\)-polymorph is symmetrically maintained in monoclinic diffraction pattern as characteristic sublattice doublet is observed between ca. 2\(\theta\) ≈ 45.9–46.5° indexed as 026 and 606 [26, 27]. For x = 0.17, the convergence of this doublet peak into a sublattice singlet indexed as 220 is the clear
Fig. 4.2: X–ray diffraction patterns for Bi$_x$Ba$_{1-x}$V$_2$O$_{11-(3x/2)-\delta}$ $(0.07 \leq x \leq 0.30)$ samples.
evidence for the stabilization of metastable orthorhombic β-phase to room temperature. However, the stabilization of tetragonal γ-phase occur for x ≥ 0.20 as reflected in the convergence of sub lattice doublet at 2θ ≈ 32.19° into a singlet indexed in the tetragonal cell as (110) [26, 28, 29].

The variation in the unit cell parameters (a, b and c) and volume (V) as a function of composition x is depicted in Fig. 4.3. It is clearly noticed that the diffraction pattern for x = 0.20 can be assigned well either to the tetragonal or orthorhombic phases.

Table 4.2 illustrates the results for the refined unit cell parameters in BIBAVOX system. The composition with x = 0.20 acts as a border line between β and γ-phase stability with mean cell (a ≈ b ≈ 3.977 Å, c ≈ 15.393 Å) and mean volume V (486.698 Å) with respect to the β-phase model, space group \(ABa2\). The general increase in c parameter with increase in barium concentration can be attributed to the substitution of smaller V\(^{5+}\) (0.59 Å) by larger Ba\(^{2+}\) (1.35 Å) in 6-fold co-ordination geometry [30, 31]. This behavior of BIBAVOX is generally typical for other BIMEVOXes also [5, 14, 29, 32–34].
Fig. 4.3: Variation in the unit cell parameters and cell volume of BIBAVOX system as a function of composition (x).
Table 4.2: Unit cell parameters for various compositions for Bi₅BaₓV₂₋ₓO₁₁₋(3ₓ/2)₋δ system.

<table>
<thead>
<tr>
<th>x</th>
<th>a( Å)</th>
<th>b( Å)</th>
<th>c( Å)</th>
<th>V( Å³)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.07</td>
<td>5.541</td>
<td>5.618</td>
<td>15.344</td>
<td>477.649</td>
<td>α</td>
</tr>
<tr>
<td>0.10</td>
<td>5.544</td>
<td>5.617</td>
<td>15.355</td>
<td>478.165</td>
<td>α</td>
</tr>
<tr>
<td>0.13</td>
<td>5.552</td>
<td>5.614</td>
<td>15.367</td>
<td>478.973</td>
<td>α</td>
</tr>
<tr>
<td>0.17</td>
<td>5.563</td>
<td>5.609</td>
<td>15.382</td>
<td>479.963</td>
<td>β</td>
</tr>
<tr>
<td>0.20</td>
<td>3.977</td>
<td>-</td>
<td>15.393</td>
<td>486.698</td>
<td>γ</td>
</tr>
<tr>
<td>0.30</td>
<td>3.983</td>
<td>-</td>
<td>15.404</td>
<td>488.606</td>
<td>γ</td>
</tr>
</tbody>
</table>
4.3.3. Differential thermal analysis (DTA)

The temperature ranges of stability of the polymorphic modifications of the solid solutions were refined by using DTA analysis (Fig. 4.4). Single endothermic peaks at 385 and 403°C for compositions $x = 0.10$ and $x = 0.13$ respectively reveal the existence of direct $\alpha \rightarrow \gamma$ phase transition as reported earlier [35]. The appearance of a single endothermic peak at 380°C for $x = 0.17$ shows $\beta \rightarrow \gamma$ phase transition, which is in agreement with XRD results. Whereas the peaks around 398 and 411°C for $x=0.20$ and $x=0.30$ respectively shows the presence of $\gamma' \leftrightarrow \gamma$ transition.

Table 4.3 lists the values of transition temperatures and the corresponding enthalpies. It is observed that the heat flow accompanied with the $\alpha \leftrightarrow \gamma$ transition per unit mass is slightly more than that required for $\beta \leftrightarrow \gamma$ transition. Such observations were also reported earlier for other BIMEVOXes [14, 35–37].

4.3.4. 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, (4.1)
Fig. 4.4: DTA thermograms of BIBAVOX system versus composition (x).
Table 4.3: Transition temperatures and enthalpies determined from DTA thermograms for the system

\[ \text{Bi}_4\text{Ba}_x\text{V}_{2-x}\text{O}_{11-(3x/2)-\delta}. \]

<table>
<thead>
<tr>
<th>x</th>
<th>( \alpha \leftrightarrow \gamma )</th>
<th>( \beta \leftrightarrow \gamma )</th>
<th>( \gamma' \leftrightarrow \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( T \ ( ^\circ C ) ) ( \Delta H \ ( \text{J.g}^{-1} ) )</td>
<td>( T \ ( ^\circ C ) ) ( \Delta H \ ( \text{J.g}^{-1} ) )</td>
<td>( T \ ( ^\circ C ) ) ( \Delta H \ ( \text{J.g}^{-1} ) )</td>
</tr>
<tr>
<td>0.10</td>
<td>385 39.17</td>
<td>- -</td>
<td>- -</td>
</tr>
<tr>
<td>0.13</td>
<td>403 38.05</td>
<td>- -</td>
<td>- -</td>
</tr>
<tr>
<td>0.17</td>
<td>- -</td>
<td>380 31.75</td>
<td>- -</td>
</tr>
<tr>
<td>0.20</td>
<td>- -</td>
<td>- -</td>
<td>398 8.16</td>
</tr>
<tr>
<td>0.30</td>
<td>- -</td>
<td>- -</td>
<td>411 4.08</td>
</tr>
</tbody>
</table>
\[ Z(\omega) = \frac{1}{B(j \omega)^n} : j = \sqrt{-1} \]  

(4.1)

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, (4.2) and (4.3) as

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

(4.2)

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

(4.3)

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

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

(4.4)

\( R_g \) and \( R_{gb} \) can be exactly calculated from the intercept of the corresponding \( Z' \)-axis. The values of angular frequencies at grain (\( \omega_g \)) and grain boundary (\( \omega_{gb} \)) are calculated from the frequency of the applied field at which the imaginary part of the impedance \( Z'' \) reaches a maximum according to equation (4.5):

\[ \omega_i = 2\pi f_{\text{max},i} \]  

(4.5)

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 [38].
The impedance plane plots of Bi$_4$Ba$_x$V$_{2-x}$O$_{11-(3x/2)-\delta}$ in the composition range $0.07 \leq x \leq 0.30$ at $t = 280^\circ$C are represented in Fig 4.5. It is clearly observed that the plots show two depressed capacitive semicircles at higher and lower frequency region, attributed to the grain and the grain boundary contribution respectively to oxygen–ionic conductivity. Whereas the inclined spike observed in the far low frequency region is associated with the impedance of the interface between the silver electrodes and the oxide-ion electrolyte [39, 40].

The values of equivalent circuit parameters calculated from the impedance plane plots are listed in Table 4.4. It is noticed that for all compositions the values of grain resistance ($R_g$) are much higher than the grain boundary resistance ($R_{gb}$) at constant temperature suggesting the major contribution of grain to ionic conductivity than grain boundary. It is also observed that with increasing composition, $R_g$ drops sharply up to $x = 0.17$ and then it increases. Similar variation is also exhibited by $R_{gb}$, indicating the role of dopant concentration on specific electrical properties of BIBAVOX material. The highest values of capacitances $C_g$ ($3.65\times10^{-12}$ F) and $C_{gb}$ ($3.57\times10^{-10}$ F) are observed for $x=0.17$, indicating the optical electrical permittivity of the sample, arises as a result of increased charge
Fig. 4.5: Impedance plane plots of BIBAVOX system for composition $0.07 \leq x \leq 0.30$ at 280 °C.
Table 4.4: Values of the equivalent circuit parameters deduced from the impedance spectra for the system \( \text{Bi}_4\text{Ba}_x\text{V}_{2-x}\text{O}_{11-(3x/2)-\delta} \) at 280 °C for compositions 0.07 ≤ x ≤ 0.30.

<table>
<thead>
<tr>
<th>x</th>
<th>( R_\text{g}(\text{k}\Omega) )</th>
<th>( C_\text{g}(\text{F}) )</th>
<th>( \tau_\text{g}(\text{s}) )</th>
<th>( R_\text{gb}(\text{k}\Omega) )</th>
<th>( C_\text{gb}(\text{F}) )</th>
<th>( \tau_\text{gb}(\text{s}) )</th>
<th>( R_\text{t}(\text{k}\Omega) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.07</td>
<td>377.67</td>
<td>1.68×10^{-12}</td>
<td>6.36×10^{-7}</td>
<td>180.09</td>
<td>1.59×10^{-10}</td>
<td>2.88×10^{-5}</td>
<td>557.76</td>
</tr>
<tr>
<td>0.10</td>
<td>195.50</td>
<td>2.16×10^{-12}</td>
<td>4.22×10^{-7}</td>
<td>87.62</td>
<td>2.91×10^{-10}</td>
<td>2.55×10^{-5}</td>
<td>283.12</td>
</tr>
<tr>
<td>0.13</td>
<td>175.89</td>
<td>2.32×10^{-12}</td>
<td>4.08×10^{-7}</td>
<td>79.39</td>
<td>2.84×10^{-10}</td>
<td>2.25×10^{-5}</td>
<td>255.28</td>
</tr>
<tr>
<td>0.17</td>
<td>101.72</td>
<td>3.65×10^{-12}</td>
<td>3.49×10^{-7}</td>
<td>46.05</td>
<td>3.57×10^{-10}</td>
<td>1.64×10^{-5}</td>
<td>147.77</td>
</tr>
<tr>
<td>0.20</td>
<td>162.91</td>
<td>2.35×10^{-12}</td>
<td>3.83×10^{-7}</td>
<td>68.11</td>
<td>2.58×10^{-10}</td>
<td>1.76×10^{-5}</td>
<td>231.02</td>
</tr>
<tr>
<td>0.30</td>
<td>233.62</td>
<td>1.70×10^{-12}</td>
<td>3.98×10^{-7}</td>
<td>118.61</td>
<td>1.53×10^{-10}</td>
<td>1.82×10^{-5}</td>
<td>352.23</td>
</tr>
</tbody>
</table>
accumulation at the grain boundaries [40]. This is also further confirmed by
the lowest values of the corresponding relaxation times $\tau_g$ and $\tau_{gb}$.

4.3.5. Temperature dependence of conductivity

Fig. 4.6 represents the Arrhenius plots of conductivities for
BIBAVOX system. For compositions $x \leq 0.13$ two line regions of different
activation energies are clearly observed, suggesting the presence of $\alpha \leftrightarrow \gamma$
phase transition which was previously confirmed by differential thermal
analysis. For $x = 0.17$ the Arrhenius plot shows two line regions with no
significant discontinuity between low and high temperature regions
revealing $\beta \leftrightarrow \gamma$ phase transition. Whereas, for $x \geq 0.20$, $\gamma' \leftrightarrow \gamma$ phase
transition is evident by the presence of single domain in the Arrhenius plot.

Fig. 4.7 shows the Arrhenius plots of conductivity for $x = 0.10$ on
heating-cooling run. Results obtained from the XRD and DTA data, suggest
that the system at this value of substitution undergoes a direct $\alpha \leftrightarrow \gamma$
transition on heating run. However, the existence of two hysteresis loops is a
clear evidence for the appearance of metastable $\beta$-phase on slow cooling. It
is interesting to note that the higher and lower temperature hysteresis loops
are correlated with the thermal stability regions of $\gamma \leftrightarrow \beta$ and $\beta \leftrightarrow \alpha$
transitions, respectively.
Fig. 4.6: Arrhenius plots of conductivity on heating for $\text{Bi}_4\text{Ba}_x\text{V}_{2-x}\text{O}_{11-}$

$\frac{(3x/2)-\delta}{(0.07 \leq x \leq 0.30)}$ samples.
Fig. 4.7: Arrhenius plots of conductivity on heating and cooling run for $x = 0.10$. 

\[ \log\sigma (S \cdot cm^{-1} \cdot K) = \frac{1000}{T (K^{-1})} \]
The 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:

$$\sigma T = D \exp\left(\frac{-E_a}{kT}\right)$$  \hspace{1cm} (4.6)

Fig. 4.8 represents the variation in the low temperature conductivity ($\sigma_{300}$) and $\Delta E_{(LT)}$ as a function of composition. The low temperature conductivity reaches a maxima for $x = 0.17$ (4.456x $10^{-5}$ S.cm$^{-1}$) followed by a decrease in activation energy, attributed to the increase in the concentration of vacancies located on equatorial lines of the perovskite layers (VO$_{3.5}$O$_{0.5}$)$^{2-}$ available for oxide-ion migration between Ba tetrahedra and Ba octahedra within the perovskite layer [41, 42]. Beyond $x = 0.17$, the conductivity gradually decreases with an increase in activation energy particularly in the composition region of $\gamma$-phase stability, which can be explained by the formation of defect pairs (e.g. Ba$^{2+}$ and V$^{\cdot\cdot\cdot}$O$^-$) i.e. the effect of higher concentration vacancies overcomes the locally ordered states [19, 43-45].

The variation in the high temperature conductivity ($\sigma_{600}$) as a function of barium concentration is presented in Fig. 4.9. It can be noted that
Fig. 4.8: Variation in the low temperature conductivity and activation energy as a function of composition (x).
Fig. 4.9: Variation in the high temperature conductivity and activation energy as a function of composition (x).
the high temperature conductivities exhibit an exponential decay with increasing barium content. This can also be reflected in the variation of the high temperature activation energy $\Delta E_{(HT)}$. The composition dependence of high temperature conductivity behavior can be attributed to the $V^{5+} \rightarrow V^{4+}$ reduction at higher temperature, which is the main conductivity trapping effect in BIMEVOX materials [41, 42]. It is also noticed that the smaller activation energy for $x=0.20$ associated with otherwise drop in the conductivity is a clear evidence for the stabilization of $\gamma$-phase.

4.4. Conclusions

In this study, it has been found that partial substitution of vanadium by barium in $\text{Bi}_4\text{V}_2\text{O}_{11-\delta}$ leads to the formation of a new member of BIMEVOX family formulated as $\text{Bi}_4\text{Ba}_x\text{V}_{2-x}\text{O}_{11-(3x/2)-\delta}$. For this substituted system the highest oxide-ionic conductivity ($4.456 \times 10^{-5}$ S.cm$^{-1}$) at 300 $^\circ$C is reported for $x = 0.17$. The high oxide-ion conductivity, in general, mainly depends on the presence of oxide ion vacancies, and these vacancies are disordered for fast ionic conduction. This ionic conductivity is mainly due to grain contribution, as evident by AC impedance spectroscopy.
References


