Abstract

Fuel cells represent a promising and viable alternate for large scale generation of electricity. Solid oxide fuel cell (SOFC) is the most advance field in the science of fuel cell due to their high efficiency than other type of fuel cells. The obstacle in the commercialization of SOFCs is their high operating temperature. Solid electrolyte is the most important part of SOFC and many efforts have been carried out to develop a suitable electrolyte, with higher ionic conductivity in intermediate temperature range (400-700°C).

Several electrolyte materials have been studied and it was found that the BIMEVOX (doped bismuth vanadates) family of oxide-ion conductors show higher conductivity at intermediate temperatures when doped with various aliovalent cations. So this family of oxide-ion conductors can be used in many technological applications like oxygen sensors, air separators and solid oxide fuel cells (SOFCs) etc.

The objective of the present work entitled “Study on effect of substitution on conductivity and phase transition in oxide ion conductors” is to demonstrate the superiority of the bismuth vanadate based solid electrolytes as compared to commonly used electrolyte materials like Yttria stabilized zirconia, doped ceria and lanthanum gallates etc.
In this study we prepared four new electrolytes namely BICAVOX, BIBAVOX, BISNVOX and BIMNVOX solid solutions by doping on the vanadium site by conventional solid state reactions. The structural properties, phase transitions and oxide-ion conductivity were calculated by using different techniques like FT-IR spectroscopy, Differential Thermal Analysis, X-ray Diffraction Analysis and AC Impedance Spectroscopy.

This thesis comprises of six chapters each one of these is described as follows.

**CHAPTER-ONE: GENERAL INTRODUCTION**

This chapter briefly describes solid electrolytes and their applications. History and classification of fuel cells on the basis of solid electrolyte used is also presented in this chapter. Different types of fuel cells that have been briefly described are:

- **(i)** Proton exchange membrane fuel cell (PEMFC)

- **(ii)** Alkaline fuel cell (AFC)

- **(iii)** Phosphoric acid fuel cell (PAFC)

- **(iv)** Molten carbonate fuel cell (MCFC)

- **(v)** Direct methanol fuel cell (DMFC)

- **(vi)** Regenerative fuel cell
Zinc air fuel cell (ZAFC)

Solid oxide fuel cell (SOFC)

Among all these fuel cells SOFCs are most important type of fuel cells as they offer pollution free technology for the generation of electricity with high efficiency.

The most important part of a fuel cell that has the highest impact on its performance is the solid electrolyte. Yttria stabilized zirconia is the most commonly used solid electrolyte in the fuel cell. It has excellent mechanical and electrical properties but suffers from the disadvantage of being operative at very high temperatures (1000°C) which is not easily achievable. So a need was felt to develop an oxide-ion conductor with high oxide-ion conductivity at intermediate temperatures. There are various families of oxide-ion conductors that fulfill the above requirements. Some of them are listed below:

(i) Fluorite type oxide-ion conductors

(ii) Bi$_2$O$_3$ based oxide-ion conductors

(iii) Doped ceria based oxide-ion conductors

(iv) Perovskite based oxide-ion conductors

(v) Brownmillerite based oxide-ion conductors
Aurivillius based oxide-ion conductors

CHAPTER-TWO: The BIMEVOX family.

This chapter briefly reviews the history and the research findings by various groups in the field of BIMEVOX family of oxide-ion conductors. Abraham et al. was the first to describe about the BIMEVOX family, which is derived from the partial substitution of vanadium in \( \text{Bi}_4\text{V}_2\text{O}_{11-\delta} \) (where \( \delta \) is the oxide-ion vacancy). The substituted compound has remarkably high oxide-ion conductivity at intermediate temperature than that of the parent compound. It was this feature of the new material, which attract many scientists towards it.

The parent compound structurally is a layered Aurivillius type of compound which can be formulated as \((\text{Bi}_2\text{O}_2)^{2+} (\text{VO}_{3.5\Box_{0.5}})^{2-}\), where \(\Box\) represents an oxide-ion vacancy in the perovskite–like slabs (vanadate layers). Depending on temperature, the \( \text{Bi}_4\text{V}_2\text{O}_{11-\delta} \) exhibits three principal phases, namely \(\alpha\) (monoclinic), \(\beta\) (orthorhombic) and \(\gamma\) (tetragonal). These polymorphic forms underwent two types of reversible phase transitions i.e. \(\alpha \leftrightarrow \beta\) at 450ºC and \(\beta \leftrightarrow \gamma\) at 560ºC. The existence of two other phases, one before melting on heating (\(\gamma'\)), and the second (\(\alpha'\)), on cooling have also been reported but these phases have never been fully characterized. Characterization techniques that have been used to investigate the phase
structures of the BIMEVOXes that are synthesized in this study are also briefly described in this chapter and these are:

(i) FT-IR Spectroscopy
(ii) X-ray Diffraction Analysis
(iii) Differential Thermal Analysis (DTA)
(iv) AC Impedance Spectroscopy

CHAPTER-THREE:

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

This chapter deals with the synthesis method and analysis of newly synthesized Bi$_4$Ca$_x$V$_{2-x}$O$_{11-(3x/2)-\delta}$ solid solutions in the composition range $0.07 \leq x \leq 0.30$. The stability of different phases as a function of composition was analyzed by X–ray powder diffraction, FT–IR spectroscopy and differential thermal analysis (DTA). For the compositions $x \leq 0.10$ monoclinic $\alpha$–phase structure is retained at room temperature. For $x = 0.13$, orthorhombic $\beta$–phase is observed, whereas for $x \geq 0.17$, high $\mathrm{O}_2$–ionic–conducting tetragonal $\gamma$–phase is stabilized. However the highest ionic conductivity $\sigma_{300^\circ\mathrm{C}} = 3.27 \times 10^{-4}$ S.cm$^{-1}$ was observed for $x = 0.17$. This higher value of conductivity of the substituted compound as compared to the parent compound can be attributed to the increased oxygen ion vacancies.
generated as a result of cation doping. AC impedance spectroscopy reveals the fact that this ionic conductivity is mainly due to the grain contribution.

CHAPTER-FOUR:

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

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 according to the substitution equation

$$2 \text{Bi}_2\text{O}_3 + x \text{BaO} + (1-\frac{x}{2}) \text{V}_2\text{O}_5 \rightarrow \text{Bi}_4\text{Ba}_x\text{V}_{2-x}\text{O}_{11-(3x/2)-\delta}$$

The polymorphism and electrical properties of these samples are studied by FT-IR spectroscopy, X-ray diffraction technique, differential thermal analysis (DTA) and AC impedance spectroscopy. The solid solutions with composition $0.07 \leq x \leq 0.13$ are isostructural with the monoclinic phase $\alpha$-Bi$_4$V$_2$O$_{11-\delta}$. However, Orthorhombic $\beta$-phase is observed for $x = 0.17$ and tetragonal $\gamma$-phase is stabilized for $x \geq 0.20$. X-ray and DTA results reveal the occurrence of $\alpha \leftrightarrow \gamma$ transition for $x \leq 0.13$, $\beta \leftrightarrow \gamma$ transition for $x = 0.17$ and $\gamma' \rightarrow \gamma$ transition for $x \geq 0.20$. AC impedance plots at $280^\circ$C for all compositions show greater contribution of grain to ionic conductivity than grain boundary. The highest ionic conductivity, $\sigma_{300^\circ C} = 4.456 \times 10^{-5}$ S.cm$^{-1}$ is observed for $x = 0.17$. The ionic conductivity of the substituted compounds
is higher than the parent $\alpha$-Bi$_4$V$_2$O$_{11-\delta}$, due to the increased oxygen-ion vacancies generated as a result of barium doping.

**CHAPTER-FIVE:**

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

Samples of Sn$^{4+}$-substituted bismuth vanadate formulated as Bi$_4$Sn$_x$V$_{2-x}$O$_{11-(x/2)-\delta}$ in the composition range $0.07 \leq x \leq 0.30$ were prepared by standard solid–state reactions. The sample characterization and the principal phase transitions; $\alpha\leftrightarrow\beta$, $\beta\leftrightarrow\gamma$ and $\gamma'\leftrightarrow\gamma$ were investigated by FT–IR spectroscopy, X–ray powder diffraction, differential thermal analysis (DTA) and AC impedance spectroscopy. For composition $x = 0.07$, $\alpha\leftrightarrow\beta$ and $\beta\leftrightarrow\gamma$ phase transitions were observed at temperatures $451$ and $536^\circ$C respectively. The endothermic peaks at $439$ and $418^\circ$C for $x = 0.13$ and $x = 0.17$ respectively show the existence of only $\beta\leftrightarrow\gamma$ phase transition. The DTA thermograms and Arrhenius plots of conductivities reveal the existence of $\gamma'\leftrightarrow\gamma$ phase transition at $411$ and $423^\circ$C for $x = 0.20$ and $x = 0.30$ respectively. AC impedance plots show that the conductivity is mainly due to the grain contribution which is evident in the enhanced short range diffusion of oxide ion vacancy in the grains with increasing temperature. The highest ionic
conductivity \((5.03 \times 10^{-5} \text{ S.cm}^{-1} \text{ at } 300^\circ\text{C})\) was observed for \(x = 0.17\) solid solution with less pronounced thermal hysteresis.

**CHAPTER-SIX:**

**Electrical conductivity and phase transition studies in Mn-doped \(\text{Bi}_4\text{V}_2\text{O}_{11-\delta}\) oxide-ion conductor.**

Ceramic solid solutions \(\text{Bi}_4\text{Mn}_x\text{V}_2-x\text{O}_{11-(x/2)-\delta}\) in the composition range \(0.07 \leq x \leq 0.30\) were obtained by solid state synthesis according to the substitution equation.

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

Structural investigations were carried out by using a combination of FT-IR and powder X-ray diffraction technique. Polymorphic transitions \((\beta \leftrightarrow \gamma \text{ and } \gamma' \leftrightarrow \gamma)\) were detected by DTA and variation in the Arrhenius plots of conductivity. The solid solutions with composition \(0.07 \leq x \leq 0.17\) are isostructural with the orthorhombic \(\beta\)-phase, and those with \(x \geq 0.20\) represent tetragonal \(\gamma\)-phase. With increasing \(\text{Mn}\) concentration, the conductivity of solid solutions increases from \(3.684 \times 10^{-6}\) \((x = 0.07)\) to \(2.467 \times 10^{-5}\) \((x = 0.17)\). AC impedance plots show that the conductivity is mainly due to the grain contribution which is evident in the enhanced short range diffusion of oxide ion vacancy in the grains with increasing temperature.