CHAPTER VII

Summery and Scope of the Future Work

7.1 Summery

In the recent past, a great deal of interest has been generated in developing novel solid-state ionic conductors at intermediate temperatures between 400 and 600 °C. The broad objective of our present research work is to study the effects of doping on bismuth vanadate to obtain a material exhibiting high oxide-ion conduction and hence establish its prospective applications in various solid state devices. In particular, this dissertation work focuses on the variation in electrical conductivity, phase transition behaviour and phase stability induced by doping at bismuth sites. As we have already mentioned that the investigation on the effects of substitution at Bi site on the microstructure and its correlation with ionic conductivity were less emphasized, we undertake to study the dependence of electrical properties and phase stabilities (polymorphic transition as well as thermal decomposition) of doped and undoped bismuth vanadate $Bi_{4-x}ME_xV_2\ O_{11-\delta}$ (ME=Li, Ca, Ba) on temperature and time for different compositions. The findings of the dissertation work are summarized as follows:

1. For the undoped compound $Bi_4V_2O_{11-\delta}$, the room temperature XRD pattern reveals α-phase of orthorhombic structure with cell parameters a = 5.521, b = 5.598 and c = 15.243.

2. The SEM micrograph of the parent compound (sintered at 800 ^{0}C) shows fairly developed grain with good grain to grain connectivity.

3. The DSC study on the undoped sample confirms $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ phase transitions. It is to be noted that all the samples studied in our research work exhibit hysteresis behaviour.

4. The conductivity of the parent compound increases with the increase of temperature. All these results fairly agree with other reported values.

3. For the monovalent metal (Li^{1+}) doped $Bi_4V_2O_{11}$ system, doped composition with x=0.1 possess orthorhombic α-superstructure and β-polymorph is found to be partially suppressed in the substitution range $x \geq 0.2$ at room temperature.

4. The conductivity of all the doped specimens is higher than the parent compound in the intermediate (380 $^{\circ}$C to 470 $^{\circ}$C) as well as in high temperature region (above 500 $^{\circ}$C). The highest conductivity (1.6×10^{-3} S cm^{-1}) with respect to the parent compound is obtained for x = 0.3 at 430 $^{\circ}$C.

5. In the low temperature region (below 380 $^{\circ}$C) also the conductivity of the doped specimen except x = 0.4 is higher than the parent compound but gradually decreases with increasing dopant concentration. This might be correlated with the increasing grain boundary contribution (sintering temperature of the samples decreases with Li content).

6. For the Ca doped system ($Bi_{4-x}Ca_xV_2O_{11-\delta}$; $0 \leq x \leq 0.4$), the compositions $0 \geq 0.3$ show orthorhombic α-phase and γ-phase is stabilized for the composition $x = 0.4$.

7. The conductivity of the samples $x \leq 0.2$ is higher than the parent compound and for $x \geq 0.3$, it is lower than the parent compound (throughout the entire temperature range, i.e., 200 - 600 °C). The highest conductivity with respect to the parent compound is observed for x=0.2 sample (Ca doped) with 1.3×10^{-3} S/ cm^{-1}at 470 ^{0}C.

8. The Ba doped series the compounds possess orthorhombic α-phase. However, α→β phase transition is partially suppressed for compositions $x \geq 0.3$.

9. In the low temperature region (below 470 °C), the conductivity of the doped specimens except x = 0.4 of Ba doped series, is found to be higher than the parent compound.

10. In the high temperature region (above 520 °C), the conductivity of x = 0.1 composition is higher than the parent compound and decreases with the increasing Ba

concentration. The highest ionic conductivity ($1.3x10^{-3}$ S/cm^{-1}) with respect to the parent compound is obtained for x = 0.1 composition at 460 ^{0}C.

11. The dielectric behaviour of Ba doped series reveals ferroelectricity in the material.

12. The modulus and ac conductivity plots obtained for the solid electrolyte systems $Bi_{4-x}Me_xV_2O_{11-\delta}$; $0 \leq x \leq 0.4$ (Me = Ca, Li, Ba) were typical and similar to those exhibited by other solid electrolyte.

13. The frequency dependent conductivity behaviour suggests that the conductivity relaxation mechanism is temperature independent.

14. The study on the electric modulus for different temperature data indicates relaxation mechanisms possess same thermal energy and the corresponding dynamical processes are temperature independent.

7.2 Scope of the future work

In this dissertation work we have investigated the effects of monovalent and divalent dopants (at Bi-site) on oxide-ion conductivity and phase stability of bismuth vanadate solid solution. The investigation on physical properties of solid electrolyte is very much important in designing a more favourable BIMEVOX. In this context, high resolution XRD and high temperature XRD (HT-XRD) analyses are suggested to be important for further understanding of oxide-ion conduction and formation of different polymorphs.

Our future work will focus on optimization of the structural and electrical behaviour of BIMEVOX system by substituting higher valance cations for Bi^{3+}. We will also continue our previous work by carrying out high temperature X-ray diffraction analyses to provide a clear insight of on the ranges of α, β and γ-phases and fitting of the impedance data to calculate the contribution from bulk and grain boundary.

List of publications

Papers published in refereed International Journals

1. **Jugananda Sut**, Lakhinath Bora and A. Pandey, Synthesis, Structure and Electrical Conductivity of Li-Substituted $Bi_4V_2O_{11}$ solid Electrolyte; *International Journal of Innovative Research & Development,* 2012, Vol.1, Issue 7, 181-185.
2. Amrit Puzari, Sharat Saurabh, Tania Bhowmik, Priyanka Basu, Prakash Kumar, Pawan Pandey**, Jugananda Sut,** Parameswar Rao Ramesh, Venkatesh Gude, Preparation and Characterization of Hydroquinone aggregate-TiO_2 Composite produced by Copper (II) Catalyzed reaction, a Promising Material for Application in Solar cell *International Journal of Innovative Research & Development,* 2012, Vol.1, Issue 7, 204-208.
3. **Jugananda Sut**, A. Pandey, Synthesis, Structure and Electrical Characterization of Barium Substituted $Bi_4V_2O_{11}$ Solid Solution **(to be communicated)**.
4. **Jugananda Sut**, A. Pandey, Structural and electrical study of $Bi_{4-x}Me_xV_2O_{11-\delta}$ (M=Li) solid solution **(to be communicated)**.
5. **Jugananda Sut**, A. Pandey, Effect of Ca Doping at Bi-Site on the Conductivity of $Bi_4V_2O_{11}$, **(to be communicated)**.

Papers presented in conferences/seminar

6. **Jugananda Sut**, Lakhinath Borah, Non polluting renewable energy source 'Solid oxide Fuel cell', Proc. of National Seminar organized by Dhakuakhana College on Oct.23-24, 2009, , pages 60-66.
7. Lakhinath Borah, Sanjay, **Juganand Sut** and A. Pandey, AC impedance analysis of $La_2Mo_{2-x}Sn_xO_{9-d}$ series of compounds, International conference on Electroceramic (**ICE 2009**), organized by University of Delhi.
8. Lakhinath Borah, **Juganand Sut**, Sanjay and A. Pandey, Effect of sintering temperature and time on the conductivity of $La_2Mo_2O_9$, National

Conference organized by Physics Association of North East (**PANE-2010**), Manipur University.

9. **Jugananda Sut**, Lakhinath Bora and A. Pandey, Synthesis, Structure and Electrical Conductivity of Li-Substituted $Bi_4V_2O_{11}$ solid Electrolyte, International Seminar and Workshop on Energy, Sustainability and Development **(ISWESD - 2012)** held on October 12-14, 2012 in the Department of Physics, Sibsagar College, Assam, India.
10. **Jugananda Sut**, Prasanta Gogoi and A. Pandey, Synthesis, Thermal and Electrical Studies of $Bi_{4-x}Ba_xV_2O_{11-\delta}$ (x=0.0, 0.1 and 0.2) Solid Solutions, International conference on Green energy & Smart Materials through Science, Technology & Management (**GESM'14**) organized by Gauhati University, Gauhati.