

## Preface

Ionic conductivity originates from the migration of ions. The solid materials which exhibit high ionic conductivity comparable with those of liquid electrolytes and molten salts are termed as solid electrolyte, superionic conductors or fast ion conductors. This type of solid electrolyte materials possesses freely moving ions (cations or anions) which can move freely from crystal lattice site to crystal site. Oxygen ion conductors are a very interesting subgroup of solid electrolyte which displays high anionic conductivity where the oxide ions ( $O^{2-}$ ) are the charge carriers. Oxygen ion conductors have been widely investigated for use in several electrochemical devices such as components of fuel cells, oxygen sensors, oxygen pumps and oxygen permeable membrane catalysts. In most of the applications high temperature is required to achieve high oxygen fluxes for efficient operation. For example, solid oxide fuel cell (SOFC), the promising power generation option utilizes YSZ (yttria stabilized zirconia) electrolyte which must be operated near  $1000^{\circ}C$ . A large number of problems such as high cost of materials, stability, compatibility and thermal degradation of the materials etc. are associated with operation at high temperature of such devices and hence hinders their broad commercialization. These facts continue to motivate the researcher for developing electrolyte materials with high ionic conductivity at intermediate temperatures ( $400-600^{\circ}C$ ).

BIMEVOX compounds derived from the parent compound  $Bi_4V_2O_{11}$  by partial substitution for vanadium/bismuth with a metal are considered as the best oxide ion conductors at moderate range of temperatures ( $400$  to  $600^{\circ}C$ ).  $Bi_4V_2O_{11}$  is structurally perovskite-related type built up from  $(Bi_2O_2)^{2+}$  layers separated by  $[VO_{3.5}O_{0.5}]$  perovskite like slabs, where o stands for oxygen ion vacancy. The high temperature  $\gamma$ -phase of the parent compound  $Bi_4V_2O_{11}$  can effectively be stabilized down to room temperature by partial substitution of V-sites by aliovalent metal ions like Cu, Co, Ti, Ni, Nb, Zr etc. A

wide range of metals can be substituted into the V-site and most of them found to stabilize the high temperature  $\gamma$ -phase at relatively low temperature. In the recent past, extensive interests have been paid for the development of novel oxygen ionic conductors at intermediate temperatures between 400 to 600°C.

In the present study a series of compound  $\text{Bi}_{4-x}\text{ME}_x\text{V}_2\text{O}_{11-\delta}$  (ME = Li, Ca, Ba) have been synthesized by solid state reaction technique. The structural characterization has been done by using XRD, FTIR, SEM/EDS and DSC. The impedance spectroscopy was used to study the impedance, dielectric behaviour, dc and ac conductivity of the systems in the temperature regime from room temperature to 600°C. In all the systems, the composition selected is  $x = 0.1, 0.2, 0.3, 0.4$ . This was undertaken because no systematic studies for substitution at Bi-site with the above metals have been reported in the literature. The broad objective of this research work is to investigate the effects of doping on bismuth vanadate (at Bi-site) and to obtain a material exhibiting high oxide-ion conduction so that it becomes an excellent technical product with better performance. In particular, this work is devoted to display the variation in phase transition behaviour, electrical conductivity and dielectric response induced by doping at bismuth sites.

The room temperature XRD patterns of all the samples show orthorhombic  $\alpha / \beta$ -phase of the parent compound except for  $x = 0.4$  of Ca doped series which possess  $\gamma$ -phase of tetragonal superstructure. In all the doped samples, the  $\alpha \rightarrow \beta$  phase transition is found to be suppressed which is also supported by DSC and conductivity measurements. The FTIR studies on the doped samples reveal local crystallographic distortions in the perovskite vanadate layers giving rise to structural phase transitions.

Chapter III describes the structural, thermal and electrical studies carried out on the system by doping with monovalent metal  $\text{Li}^{1+}$  which notably changed the physical as well as the electrical properties. The parent as well as the doped composition with  $x=0.1$  possess orthorhombic  $\alpha$ -superstructure and  $\beta$ -polymorph is partially suppressed in the substitution range  $x \geq 0.2$  at room temperature. It has been observed that, the conductivity of all the doped specimens is higher than the parent compound in the intermediate (380 °C to 470 °C) as well as in high temperature region (above 500 °C). In the low

temperature region (below 380 °C), decrease of conductivity is observed with increasing dopant concentration which might be attributed to increasing grain boundary contribution due to gradual decrease of sintering temperature (sintering temperature of the samples decreases with Li content). On the other hand, higher ionic conductivity for the substituted phases as compared to the parent compound can be correlated with the increasing oxygen vacancies created by aliovalent substitution. The highest conductivity with respect to the parent compound is obtained for  $x = 0.3$  at 430 °C.

Doping with divalent metals Ca and Ba at Bi-site on the parent compound  $\text{Bi}_4\text{V}_2\text{O}_{11}$  with the general formula  $\text{Bi}_{4-x}\text{ME}_x\text{V}_2\text{O}_{11-\delta}$  (ME = Ca, Ba) is carried out to investigate the structural and electrical properties of the systems. The detailed study by XRD, DSC and electrical conductivity measurements for Ca doped series reveal orthorhombic  $\alpha$ -phase for the compositional range  $x \leq 0.3$  with partial suppression of  $\alpha \rightarrow \beta$  phase transition for  $x = 0.3$  and stabilization of tetragonal  $\gamma$ -phase for  $x = 0.4$ . Similarly, for the Ba doped series the compounds show orthorhombic  $\alpha$ -phase with partial suppression of  $\alpha \rightarrow \beta$  phase transition for  $x \geq 0.3$ . The observed impedance spectra for both the systems are similar to those other BIMEVOXes. For Ca doped system, 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  $1.3 \times 10^{-3} \text{ S/cm}^{-1}$  at 470 °C. On the other hand, except for the composition  $x = 0.4$  of Ba doped series the temperature dependent d.c. conductivity of the doped specimens is found to be higher than the parent compound in the low temperature region (below 470 °C). In the high temperature region (above 520 °C), the conductivity of all the compounds except  $x = 0.1$  is lower than the parent compound and decreases consistently with the increasing dopant concentration. The highest ionic conductivity ( $1.3 \times 10^{-3} \text{ S/cm}^{-1}$ ) with respect to the parent compound is obtained for  $x = 0.1$  composition at 460 °C. The increase of ionic conductivity could be correlated with the increasing oxygen ion vacancies and decrease of conductivity with increasing  $x$  could be explained as a result of defect pair formation.

The study of dielectric behaviour (for Ba doped series) reveals strong low frequency dispersion of dielectric constants (both  $\epsilon'$  and  $\epsilon''$ ) which suggests ferroelectricity in the material. It has been observed that at a certain frequency,  $T_c$  decreases with increase in dopant concentration. The appearance of anomaly in the temperature (T) vs.  $\log \epsilon_r$  plot near the transition temperature reveals a coupling between space charge and ferroelectricity.

The electrical behaviour of solid electrolyte systems  $\text{Bi}_{4-x}\text{Me}_x\text{V}_2\text{O}_{11-\delta}$ ;  $0 \leq x \leq 0.4$  (Me = Ca, Li, Ba) were further analyzed by using ac conductivity and complex modulus. For both pure and doped compounds the frequency dependent conductivity plots ( $\log \omega$  vs.  $\log \sigma_{ac}$ ) show three distinct regime a) low frequency dispersed b) an intermediate plateau and c) conductivity dispersion at high frequency which is a typical frequency dependent conductivity spectrum exhibited by solid electrolyte. At very low frequencies, more and more charges are accumulated at the electrode-electrolyte interface and as a result drop in conductivity is observed. In the intermediate frequency plateau region, the conductivity ( $\sigma_0$ ) is found to be frequency independent and is almost equal to dc conductivity which originates from the random diffusion of the charge carriers through activated hopping. At the high frequency region, the conductivity increases with frequency. In the plots of  $\log \omega$  vs.  $\log \sigma_{ac}$ , the frequency at which the dispersion region starts from the dc conductivity plateau is termed as hopping frequency or cross over frequency ( $\omega_0$ ). With rise in temperature, the hopping frequency shifts towards the higher frequency. For all compositions, the scaled plots ( $\log \omega/\omega_0$  vs.  $\log \sigma_{ac}/\sigma_0$ ) at various temperatures merge to a single plot which suggests that the conductivity relaxation mechanism is temperature independent. In the plots for imaginary part of modulus vs.  $\log$  of frequency i.e.,  $\log \omega$  vs.  $M''$ , the imaginary part of the electric modulus is associated with a clearly resolved peak at unique frequency which shifts towards high frequency region with the increase of temperature. These peaks are a sign of transition from long range to short range mobility of oxygen ions. Except for the composition  $x = 0.4$  of Ca doped series, all the normalized plots of electric modulus ( $\log \omega/\omega_{max}$  vs.  $M''/M''_{max}$ ) for different temperatures data superimposed on each other which indicates that relaxation

mechanisms associated with different frequencies possess the same thermal energy and the corresponding dynamical processes are temperature independent. On the other hand a diffused peak observed in the middle frequency region for  $x = 0.4$  composition of Ca doped compound can be correlated with the dominant grain boundary contribution as evident in the  $M'$  versus  $M''$  plot.