

# Investigation on Phase Stability and Electrical Properties $\text{Bi}_2\text{V}_{1-x}\text{Bi}_x\text{O}_{5.5-x/2}$ (BIBIVOX) Solid Electrolyte for Intermediate Temperature – Solid Oxide Fuel Cells (IT-SOFCs)

Elyas Sadeq Alaghbari<sup>1</sup>, Sameh Abdulgalil Shaher Alariqi<sup>1,\*</sup>,  
Niyazi Abdulmawla Sallam Al-Areqi<sup>1</sup>, Saba Beg<sup>2</sup>, Faria Khan Naqvi<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Applied Science, Taiz University, Taiz, Republic of Yemen

<sup>2</sup>Solid-State Chemistry Lab, Physical Chemistry Division, Department of Chemistry, Aligarh Muslim University, Aligarh, India

## Email address:

samehalariqi@yahoo.com (S. A. S. Alariqi)

\*Corresponding author

## To cite this article:

Elyas Sadeq Alaghbari, Sameh Abdulgalil Shaher Alariqi, Niyazi Abdulmawla Sallam Al-Areqi, Saba Beg, Faria Khan Naqvi. Investigation on Phase Stability and Electrical Properties  $\text{Bi}_2\text{V}_{1-x}\text{Bi}_x\text{O}_{5.5-x/2}$  (BIBIVOX) Solid Electrolyte for Intermediate Temperature – Solid Oxide Fuel Cells (IT-SOFCs). *American Journal of Chemical Engineering*. Vol. 5, No. 6, 2017, pp. 169-176. doi: 10.11648/j.ajche.20170506.19

Received: April 14, 2017; Accepted: May 5, 2017; Published: December 20, 2017

**Abstract:** The solid-state fuel cell is the most widely adopted energy-generating technology in the world for which different oxide-ion conductors of perovskite structures have been recently investigated for the application in the intermediate temperature-solid oxide fuel cells (IT-SOFCs). In the present work, samples of single substituted BIMEVOX i.e., BIBIVOX ( $\text{Bi}_2\text{V}_{1-x}\text{Bi}_x\text{O}_{5.5-x/2}$ ) were prepared in the composition range  $0 \leq x \leq 0.20$  using bottom up sol-gel method. XRPD, FT-IR, DTA, SEM, EDS, and AC impedance spectroscopy were used for the investigation of the correlation between the structural phase stability and oxide-ion performance of the BIBIVOX materials. It has been found that orthorhombic,  $\beta$ , and incommensurate tetragonal,  $\gamma'$ -phases were stabilized at room temperature for compositions with  $x=0.15$  and  $x=0.20$ , respectively. The enthalpy of  $\beta$ - $\gamma$  and  $\gamma'$ - $\gamma$  transition exhibited a general drop with increasing Bi content. The higher value of conductivity of the substituted compound as compared to the parent compound can be attributed to the increased oxygen 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.

**Keywords:** BIBIVOX, Phase Transitions, Ac Impedance, Ionic Conductivity

## 1. Introduction

Conduction in solid electrolytes is mainly due to the migration of whether cations or anions, but generally not both like liquid electrolytes. Recently, a wide range of solid electrolytes has received much attention due to their potential applications in many devices, oxygen sensors and also in solid batteries [1]. The most recent application of solid electrolytes is in fuel cells, especially solid oxide fuel cells (SOFCs). Bismuth oxide and its solid solutions have been considered to be promising candidates as oxide-ion solid electrolytes, because of their potential to exhibit at intermediate temperatures (300°C–500°C) high oxide-ion

conductivities [2–4].

BIMEVOXes are divalent substituted systems with general formula  $\text{Bi}_2\text{ME}_x\text{V}_{1-x}\text{O}_{5.5-x/2}$ , which are produced from a ternary solid solutions of  $\text{Bi}_2\text{O}_3$  with  $\text{V}_2\text{O}_5$  and usually transition-metal oxides. The parent compound of this family of solid electrolyte,  $\text{Bi}_4\text{V}_2\text{O}_{11}$ , structurally belongs to a layered Aurivillius-type of compounds. These Aurivillius compounds have an inter growth of  $(\text{Bi}_2\text{O}_2)^{2+}$  layers and perovskite-like slabs  $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$  that contains oxide-ion vacancies ( $\square$ ) in the perovskite-like slabs  $(\text{VO}_{3.5}\square_{0.5})^{2-}$ . The BIMEVOX family of oxide-ion conductors, based on cation substitution

of vanadium in  $\text{Bi}_4\text{V}_2\text{O}_{11}$  [5, 6] is a recently discovered Aurivillius family with high oxide-ion conductivity. BIMEVOXes upon doping or increasing temperature can exhibit three phases, such as  $\alpha$  (monoclinic),  $\beta$  (orthorhombic) and  $\gamma$  (tetragonal) with two reversible phase transformations among these different crystal structures [7–10].

It is well-known that Bi(III) ions in bismuthate layers have no contribution to the ionic conductivity of BIMEVOXes, merely dopant metal ions of different aliovalency, either singly or doubly substituted for V-site in the perovskite-like slabs do so [11, 12]. So the present study aims to illustrate not only the influence of substitution of trivalent metal ion for V(V) on the phase stabilization and electrical performance of BIMEVOX, but also the possibility of doping excess Bi(III) ions in the oxide-ion vacancies of the perovskite-like slabs. In the present work, samples of single substituted BIMEVOX i.e., BIBIVOX ( $\text{Bi}_2\text{V}_{1-x}\text{Bi}_x\text{O}_{5.5-x/2}$ ) were prepared in the composition range  $0 \leq x \leq 0.20$  using ethylene glycol-citrate sol-gel method [13]. The correlation between the structural phase stability and oxide-ion performance of the BIBIVOX materials was investigated using many advanced techniques, such as XRPD, FT-IR, DTA, SEM, EDS, and AC impedance spectroscopy.

## 2. Experimental

### 2.1. Synthesis Procedure

Samples of  $\text{Bi}_2\text{V}_{1-x}\text{Bi}_x\text{O}_{5.5-x/2}$  in the composition range  $0.05 \leq x \leq 0.20$  were prepared by using analytical grade  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{NH}_4\text{VO}_3$  as starting materials. The samples were synthesized by bottom up sol-gel method. The sol-gel method is convenient way to manufacture non-agglomerated ceramics and also helps to reduce sintering temperature. In this method, a 0.2 M citric acid is used as a chelating agent which is made in distilled water and ethylene glycol mixture at volumetric ratio of 3:1. Under constant stirring, ammonia ( $\text{NH}_3$ ) solution was added to maintain pH of the sol to neutral. Finally, obtained xerogel was dried at  $90^\circ\text{C}$  for 12 hours.

The dried xerogel was thoroughly mixed in an agate mortar for further homogenization and then thermally calcined in a muffle furnace for 5 hrs at  $550^\circ\text{C}$ . After the complete calcination, samples of BIBIVOX at room temperature were pelletized into a cylindrical shape with constant dimensions (15 mm in diameter and 2.4 to 3.1 mm thickness) under isostatic pressure of 425 MPa (Spectralab SL-89). The pellets were then sintered in air at  $650^\circ\text{C}$  for 5hrs.

### 2.2. Crystallography

The structural properties of as calcined samples of BIBIVOX system were characterized by the X-ray powder diffraction (XRPD) using a Philips PW 1050/30 X-Ray Diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda=1.54060 \text{ \AA}$ ). The diffracted beams were collected in a  $2\theta$  range  $5-80^\circ$  with an increment of  $0.020^\circ$  at a scan rate of 32.8 seconds/step. The unit cell parameters were calculated by the Reitveld

refinement method using an X'Pert Plus software program.

### 2.3. Differential Thermal Analysis

The differential thermal analysis (DTA) measurements were carried out by Schimatzu SC-TA 60 thermal analyzer. The powdered sample was heated from  $40^\circ\text{C}$  to  $740^\circ\text{C}$  at constant heating rate of  $10^\circ\text{C}/\text{min}$ . The experiments were run in nitrogen atmosphere supplied at a flow rate of 100 ml/min.

### 2.4. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

The morphologies and microstructures of as-calcined samples were examined by scanning electron microscopy using a SEM model, JEOL-6510LV SEM. From energy dispersive X-ray spectrometry (EDS) used with SEM, the corresponding EDS profiles scanned over a full scale up to 20 kV were also taken for investigating the chemical compositions of the samples and checking their purity.

### 2.5. Electrical Characterization

Electrical properties were measured by means of AC impedance spectroscopy using a Wayne Kerr 4100 LCR meter operated in the frequency range 1Hz – 1MHz operated with an AC signal of  $\sim 50 \text{ mV}$ . For AC impedance measurements, all the sintered pellets were made conducting by applying chemically pure silver paste on both pellet surfaces and finally fired at  $700^\circ\text{C}$  for 2 hrs. The experiments were run in air at every  $20^\circ\text{C}$  interval from  $100^\circ\text{C}$  to  $600^\circ\text{C}$  with a 20 min thermal equilibration before each measurement. Impedance spectra were subjected to non-linear least squares fitting using a Zview software program.

## 3. Results and Discussion

### 3.1. X-Ray Crystallography

The variation of XRPD patterns of the BIBIVOX.17 xerogel with calcination temperature for 5 hrs is presented in Figure 1. As expected from our previous works [13, 14], the sample obtained after calcined at  $450^\circ\text{C}$  for 5 hrs is still amorphous and could completely be converted into a crystalline phase upon calcinating at  $550^\circ\text{C}$ . The existence of a characteristic singlet diffraction peak 110 around  $2\theta \sim 32.5^\circ$  is a clear evidence for the crystallization of stabilized  $\gamma$ -tetragonal phase.

Figure 2 illustrates XRPD patterns of the BIBIVOX system as a function of Bismuth substitution. All the diffraction patterns for the compositions  $x < 0.17$  appear to be identical to the characteristic  $\beta$ -phase diffraction pattern observed for most of the single substituted BIMEVOXes, indicating no significant polymorphism occurs with the increase of Bi content upto  $x=0.13$ . This can be evidenced by the existence of doublet sublattice peak, indexed as (020) and (200) at  $2\theta \sim 32^\circ$ , characteristic to the orthorhombic symmetry with a space group,  $Acam$ . In the composition range  $0.17 \leq x \leq 0.20$ , the low temperature  $\gamma'$ -tetragonal phase in space group,  $14/mmm$  is stabilized, which is definitely clear from the appearance of a

singlet sublattice peak indexed as (110) at approximately the same diffraction angle [15].

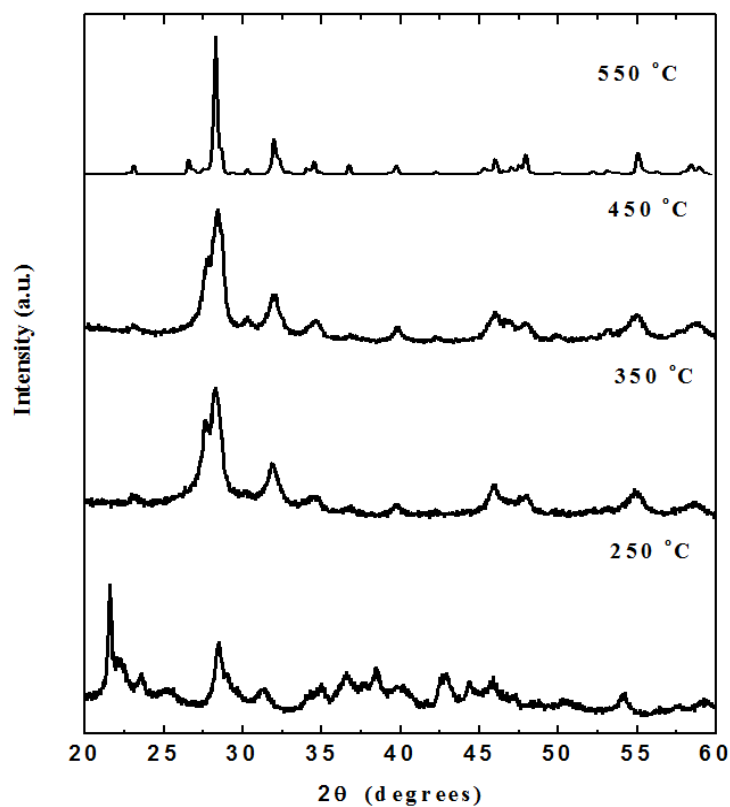


Figure 1. XPRD patterns of BIBIVOX.17 xerogel calcined at different temperatures for 5 hrs.

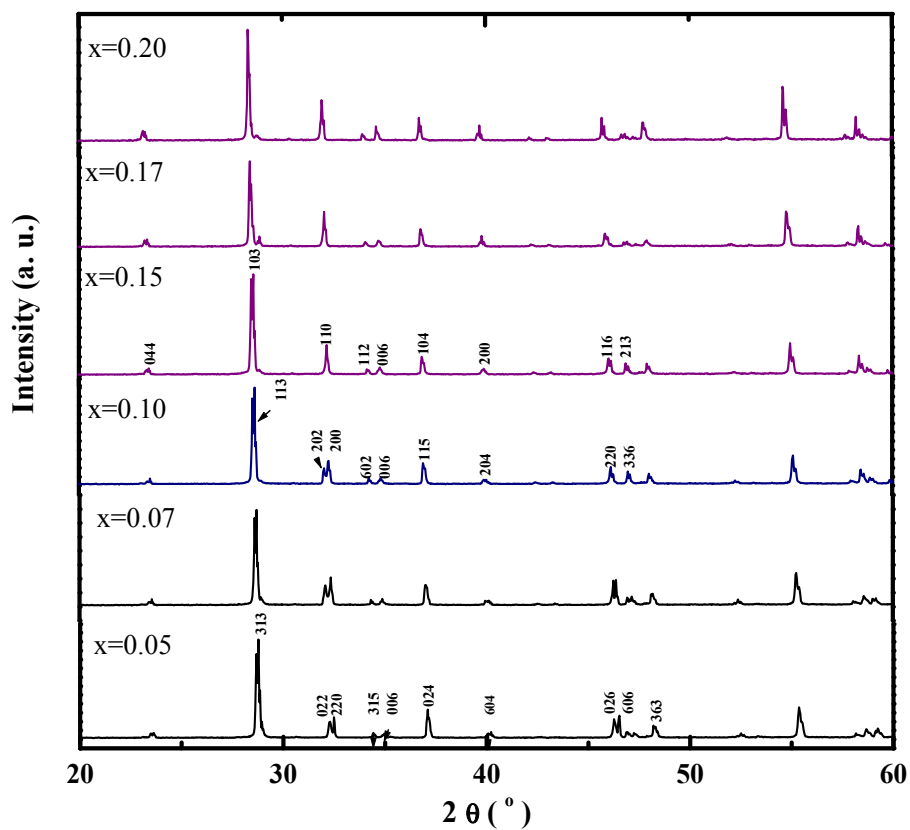


Figure 2. XPRD patterns of as-prepared BIBIVOX samples in the composition range  $0.05 \leq x \leq 0.20$ .

The variation of unit cell parameters with Bi content is illustrated in Table 1. The substitution of Bi into the parent compound,  $\text{Bi}_2\text{VO}_{5.5}$  causes an increase in the unit cell parameters. This is attributed to the incorporation of Bi (IV) of larger ionic radius (1.03 Å) into V-sites (0.54 Å) of

perovskite vanadate layers [16]. The variation of the average crystallite size and crystallographic and relative density with Bi content (Table 1) are also in a good agreement with the positive contribution of Bi substitution to the overall lattice expansion.

Table 1. Refined unit cell parameters and phase stabilizations of the BIBIVOX system.

$x$	Unit cell parameters				Phase stabilization		R-factors	
	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	Phase	Space group	$R_p$ (%)	$R_{wp}$ (%)
0.07	5.554(3)	5.611(4)	15.328(4)	477.67(4)	$\beta$	$Acam$	8.23	6.44
0.10	5.564(3)	5.603(2)	15.336(5)	478.10(3)	$\beta$	$Acam$	8.34	7.29
0.13	5.566(2)	5.592(3)	15.343(2)	477.55(4)	$\beta$	$Acam$	7.98	8.32
0.17*	5.578(3)	—	15.356(2)	478.50(3)	$\gamma'$	$I4/m\ mm$	8.75	6.91
0.20*	5.591(2)	—	15.379(2)	480.74(3)	$\gamma'$	$I4/m\ mm$	8.67	7.43
0.30*	5.607(3)	—	15.386(3)	483.71(3)	$\gamma'$	$I4/m\ mm$	7.92	6.12

\* The tetragonal lattice parameter ( $a_T$ ) was converted into the mean orthorhombic dimension ( $a_\beta$ ) using the relation:  $a_\beta = a_T/\sqrt{2}$ . Estimated standard deviations for refined lattice parameters are given in parentheses.

### 3.2. Differential Thermal Analysis

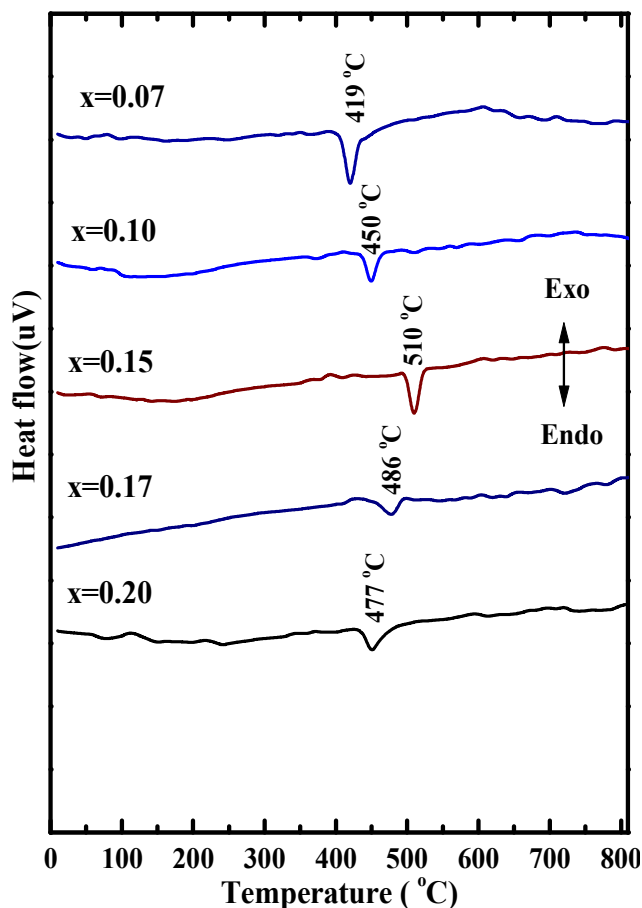


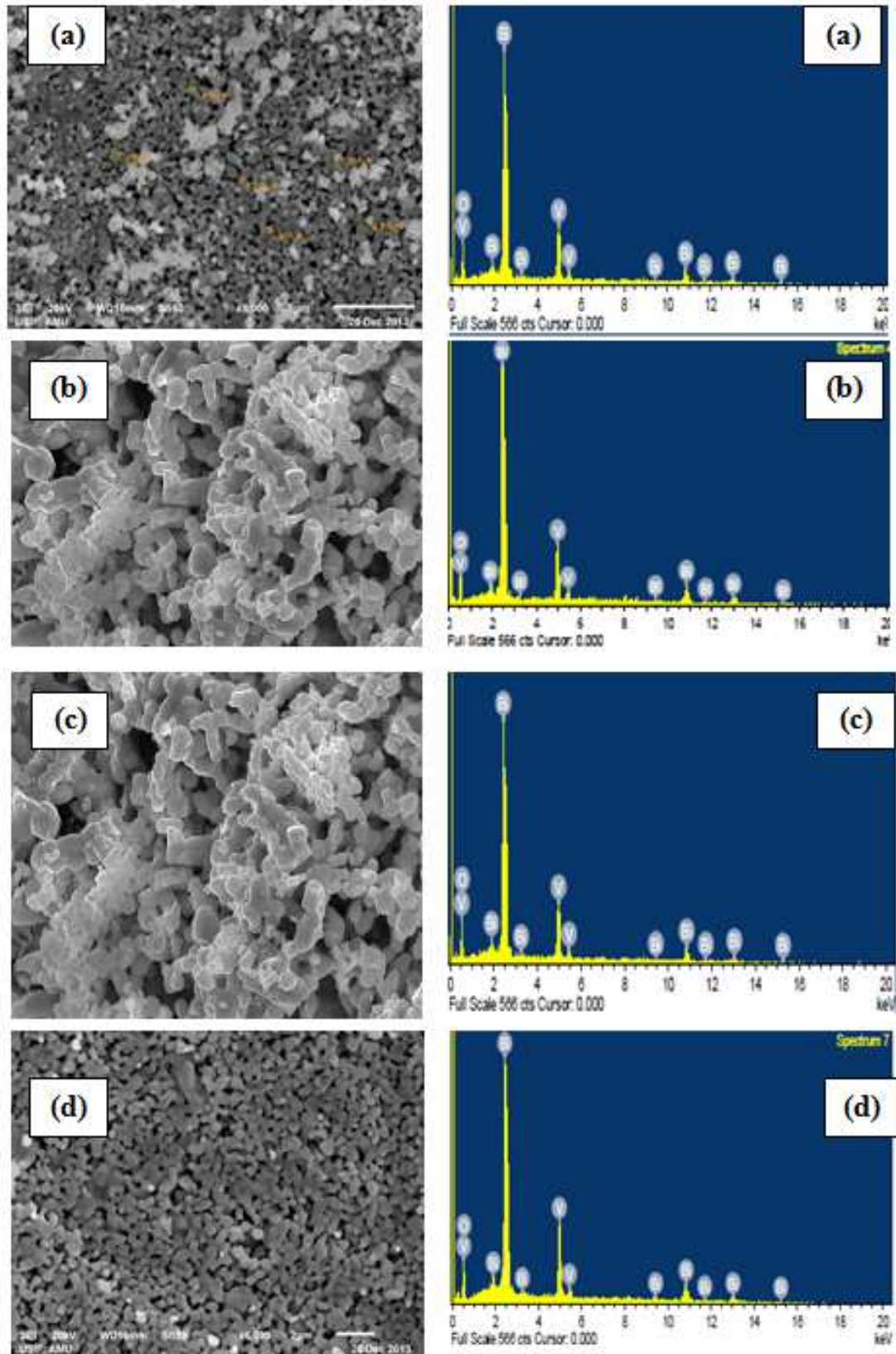
Figure 3. DTA thermograms of BIBIVOX system for various compositions.

DTA thermograms are presented in Figure 3. A single endothermic peak is observed in the temperature range 400 – 550°C for all investigated compositions. However, the

relatively large endothermic peaks seen in the DTA thermograms for  $x \leq 0.17$  are assigned to  $\beta \rightarrow \gamma$  transitions, while the occurrence of order  $\rightarrow$  disorder,  $\gamma' \rightarrow \gamma$  transition is detected in the composition range  $0.17 \leq x \leq 0.20$ . This assignment is in a good agreement with the results obtained from the XRPD analysis. It can be noted that the onset phase temperature,  $T_i$  initially increases as the a function of Bi substitution, reaching a maximum for the composition  $x=0.15$  ( $T_i=510^\circ\text{C}$ ) and thereafter it is substantially decreased in the composition range with stabilized  $\gamma'$ - BIBIVOX phase. However, the maximum  $T_i$  accompanied with increased heat flow for  $x=0.15$  might be attributed to a subtle ordering in some oxygen sublattice positions located in the perovskite-layered polyhedra [17–19].

### 3.3. SEM-EDS Analyses

The SEM images along with the corresponding EDS profiles of as-calcined samples of BIBIVOX system for different compositions are shown in Figure 4. It is clearly seen that all the samples calcined at  $600^\circ\text{C}$  are generally composed of the agglomerated particles with different shapes varying from uniform spherical to disc-like. The disc-like particles might be formed by splitting of spherical particles due to thermal effect during the prolong calcination applied. From these images it is estimated that the average particle size of bulk BIBIVOX is around ca. 0.4  $\mu\text{m}$ . In addition, EDS profiles (Figure 4) shows all the expected peaks for Bi, V and O at their normal energies [20] without any impurity peak. For all the investigated compositions, the ratio of doped Bi to V content,  $x\text{Bi}/(1-x)\text{V}$ , obtained from EDS is found to vary in a good agreement with the calculated ratio as applied in the preparation of xerogels.



**Figure 4.** SEM images (left) and EDS profiles (right) of BIBIVOX system for different compositions; (a)  $x=0.10$ , (b)  $x=0.13$ , (c)  $x=0.15$ , and (d)  $x=0.20$ .

### 3.4. Impedance Spectroscopy

The capacitances,  $C_g$  and  $C_{gb}$ , and the relaxation time,  $\tau_g$

and  $\tau_{gb}$ , at the grain and grain boundary can be obtained by the equations (1) and (2),

$$C_i = \frac{1}{R_i \omega_i} \quad (1)$$

$$\tau_i = \frac{1}{\omega_i} = C_i R_i \quad (2)$$

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

$$R_t = R_g + R_{gb} \quad (3)$$

$R_g$  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):

$$\omega_i = 2\pi f_{\max,i} \quad (4)$$

where,  $f_{\max,i}$  is the frequency at maxima of the grain ( $i \equiv g$ ) and in the grain boundary ( $i \equiv gb$ ) semicircles, respectively [21, 22].

Complex impedance spectra of BIBIVOX solid solutions at four different temperatures are shown in Figure 5. It can be noticed that for all temperatures, two capacitive semicircles are obtained. 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. 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 [10].

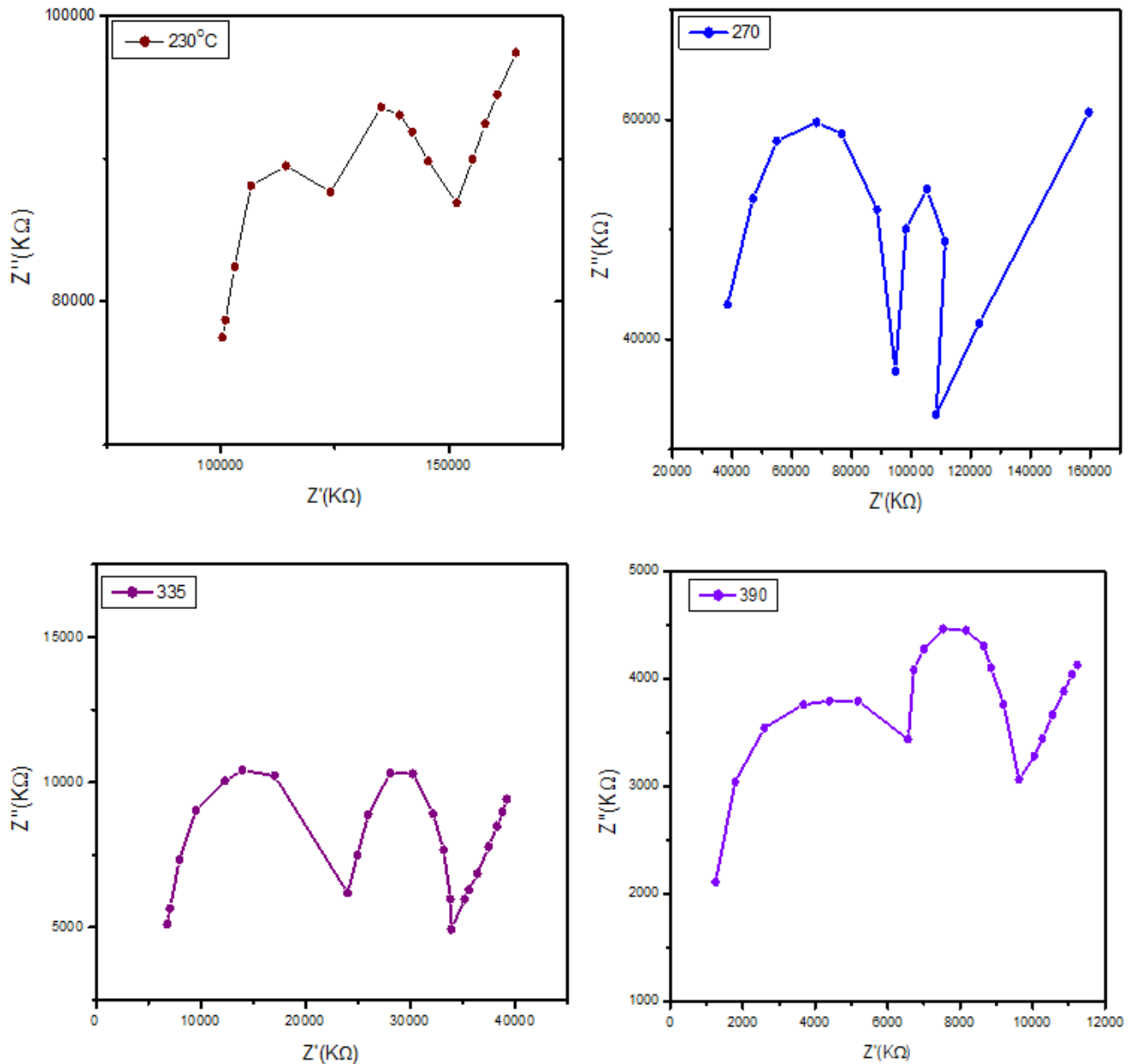
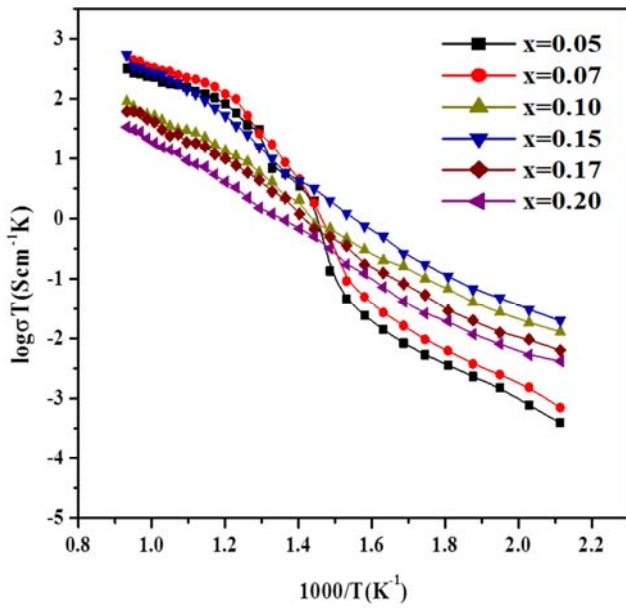


Figure 5. Impedance plane plots of BIBIVOX system for composition  $x=0.17$  at four different temperatures.





**Figure 6.** Arrhenius plots of conductivity on heating for BIBIVOX system in the composition range  $0.05 \leq x \leq 0.20$ .

Table 2 summarizes the values of equivalent circuit parameters for both grain and grain boundary contribution estimated from the impedance plane plots for  $x = 0.17$  at four different temperatures. It is clearly noticed that the values of  $R_g$  at different temperatures are higher than that of  $R_{gb}$  at the same temperature. The highest value of capacitance at grain,  $C_g$ , is  $2.47 \times 10^{-4}$  F and at grain boundary,  $C_{gb}$ , is  $3.78 \times 10^{-3}$  F found to be at  $390^\circ\text{C}$  revealing more polarisability of the solid solution at this temperatures [23].

**Table 2.** AC impedance plane plots of BIBIVOX system for composition  $x=0.17$  at different temperatures.

$T (^{\circ}\text{C})$	$R_g(k\Omega)$	$C_g(\text{F})$	$R_{gb}(k\Omega)$	$C_{gb}(\text{F})$	$R_t(k\Omega)$
230	29.422	$2.11 \times 10^{-5}$	31.02	$2.79 \times 10^{-5}$	60.44
270	54.720	$2.7 \times 10^{-4}$	11.84	$2.08 \times 10^{-4}$	66.56
335	16.929	$2.0 \times 10^{-4}$	09.82	$2.89 \times 10^{-4}$	26.75
390	05.322	$2.47 \times 10^{-3}$	03.05	$3.78 \times 10^{-3}$	08.37

### 3.5. Temperature Dependence of Conductivity

The electrical conductivity of the prepared samples was calculated from the sum of grain and grain boundary resistances, using the relation:

$$\sigma = 1 / (R_t \times (L/A)) \quad (5)$$

Where,  $(L/A)$  is the ratio of thickness to cross section area of the sintered pellet. The temperature dependences of conductivity were computed by using the Arrhenius equation:

$$\sigma T = A \exp(\Delta E/kT) \quad (6)$$

Figure 6 depicts the Arrhenius plots of conductivity of BIBIVOX system in the composition range  $0.05 \leq x \leq 0.20$ . For compositions  $0.05 \leq x \leq 0.07$ , two line regions with

different slopes are observed which ascribe to the presence of  $\alpha \leftrightarrow \beta$ , and  $\beta \leftrightarrow \gamma$  phase transitions. Whereas the existence of order-disorder  $\gamma' \leftrightarrow \gamma$  phase transition for  $x \geq 0.17$  is confirmed by the existence of single line region with no significant discontinuity between low and high temperature regions. There is merely a point at which activation energy changes. The above results were also previously confirmed by XRPD and DTA analyses.

## 4. Conclusion

In  $\alpha\text{-Bi}_4\text{V}_2\text{O}_{11}$  single substitution of V by Bi stabilizes the high temperature tetragonal  $\gamma'$ -phase at room temperature for compositions  $x=0.17$  and  $x=0.20$ . While the stabilization of orthorhombic  $\beta$ -phase is observed for compositions  $0.10 \leq x \leq 0.15$ . It was found that the substituted compound has pronounced ionic conductivities, i.e.,  $1.66 \times 10^{-3} \text{ S.cm}^{-1}$  at  $300^\circ\text{C}$  and  $1.78 \times 10^{-3} \text{ S.cm}^{-1}$  at  $600^\circ\text{C}$ . The enhancement of thermal phase stability, low temperature electrical properties, and short-range diffusion is a clear evidence for a good electrolytic performance of the stabilized  $\gamma'$ -phases. These interesting features make BIBIVOX a potential solid electrolyte for application in many of the electrochemical devices operating at moderate temperatures, particularly IT-SOFCs.

## References

- [1] B. C. H. Steele, High Conductivity Solid Ionic Conductors, Recent Trends and Applications, ed. T. Takahashi, World Scientific, Singapore, 1989.
- [2] T. Takahashi, H. Iwahara and T. Arao. *J Appl Electrochem* 1975; 5: 187.
- [3] N. M. Sammes, G. A. Tompsett, H. Nafe and F. Aldinger. *J Eur Ceram Soc* 1999; 19: 1801.
- [4] V. V. Kharton, F. M. B. Marques and A. Atkinson. *Solid State Ionics* 2004; 174: 135.
- [5] F. Abraham, M. F. Debreuille-Gresse, G. Mairesse and G. Nowogrocki. *Solid State Ionics* 1988; 28–30: 529.
- [6] F. Abraham, J. C. Boivin, G. Mairesse and G. Nowogrocki, *Solid State Ionics* 1990; 40–41: 934.
- [7] E. Pernot, M. Anne, M. Bacmann, P. Strobel, J. Fouletier, G. Mairesse, F. Abraham and G. Nowogrocki. *Solid State Ionics* 1994; 70–71: 259.
- [8] O. Joubert, A. Jouanneaux, M. Ganne, R. N. Vannier and G. Mairesse. *Solid State Ionics* 1994; 73: 309.
- [9] S. Beg, N. A. S. Al-Areqi and S. Haneef. *Solid State Ionics* 2008; 179: 2260.
- [10] S. Beg, S. Hafeez and N. A. S. Al-Areqi. *Solid State Ionics* 2014; 261: 125.
- [11] S. Beg, N. A. S. Al-Areqi, A. Al-Alas and S. Hafeez. *Ionics* 2014; 20: 269.

- [12] S. Beg, N. A. S. Al-Areqi, S. Hafeez and A. Al-Alas. *Ionics* 2015; 21:421.
- [13] A. Al-Alas, S. Beg, N. A. S. Al-Areqi and S. Hafeez. *J Eur Ceram Soc* 2013; 33: 2111.
- [14] S. Beg, A. Al-Alas and N. A. S. Al-Areqi. *J Alloys Compds* 2010; 504: 413.
- [15] M. Huve, R. N. Vannier, G. Nowogrocki, G. Mairesse, G. V. Tendeloo. *J Mater Chem* 1996; 6: 1339.
- [16] R. D. Shannon. *Acta Crystallogr* 1976; A 32: 751.
- [17] S. Lazure, R. N. Vannier, G. Nowogrocki, M. Anne and P. Strobel. *J Mater Chem* 1995; 5: 1395.
- [18] N. S. A. Al-Areqi, S. Beg and A. Al-Alas. *J Phys Chem. Solids* 2012; 73: 730.
- [19] O. Joubert, M. Ganne, R. N. Vannier and G. Mairesse. *Solid State Ionics* 1996; 83: 199.
- [20] A. Zhang and J. Zhang. *J Hazard Mater* 2010; 173: 265.
- [21] M. Guillodo, J. Fouletier, L. Dessemond and P.D. Gallo. *J Eur Ceram Soc* 2001; 21: 2331.
- [22] M. J. Godinoh, P. R. Bueno, M. O. Orlandi, E. R. Leite and E. Longo. *Mater Lett* 2003; 57: 2540.
- [23] A. Kezionis, W. Bogusz, F. Krok, J. Dygas, A. Orliukas, I. Abrahams and W. Gebicki. *Solid State Ionics* 1999; 119: 145.