Ionic Conductivity of $Bi_2Ni_xV_{1-x}O_{5.5-3x/2}$ ($0.1 \leq x \leq 0.2$) Oxides Prepared by a Low Temperature Sol-Gel Route

Rolan Rusli[1], Isaac Abrahams[2], Aep Patah[1], Bambang Prijamboedi[1], and Ismunandar[1,*]

[1]*Inorganic and Physical Chemistry Division, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia*
[2]*Materials Research Institute, School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom*
* Email: ismu@chem.itb.ac.id*

Abstract. Solid oxides fuel cells (SOFCs) is one technology that could contribute toward future sustainable energy. One of the most important components of an SOFC is the electrolyte, which must have high ionic conductivity. Cation substitution of vanadium in $Bi_4V_2O_{11}$ yields a family of fast oxide ion conducting solids known collectively as the BIMEVOXes (bismuth metal vanadium oxide), which have the potential to be applied as electrolytes in SOFCs. The purpose of this work is to study the effect of Ni concentration, when used as a dopant, on the ionic conductivity of $Bi_2Ni_xV_{1-x}O_{5.5-3x/2}$ (BINIVOX) oxides ($0.1 \leq x \leq 0.2$) when prepared by a sol gel method. The gels were calcined at 600 °C for 24 h to produce BINIVOX. These oxides were found to exhibit the γ-phase structure with tetragonal symmetry in space group *I4/mmm*. Ionic conductivity of BINIVOX at 300 °C were 6.9×10^{-3} S cm^{-1}, 1.2×10^{-3} S cm^{-1}, and 8.2×10^{-4} S cm^{-1}, for $x = 0.1$; 0.15; and 0.2; respectively; and at 600 °C were 1.1×10^{-1} S cm^{-1}, 5.3×10^{-2} S cm^{-1}, and 2.8×10^{-2} S cm^{-1}, for $x = 0.1$; 0.15; and 0.2; respectively.

Keywords: BIMEVOX, BINIVOX, sol gel, ionic conductivity
PACS: 88.30.M-

Introduction

Research on Aurivillius layered structures as electrolytes in solid oxides fuel cells (SOFCs) materials is an interesting topic since Abraham *et al.* reported high ionic conductivity in $Bi_4V_2O_{11}$ [1] at temperatures above 600°C. On cooling, $Bi_4V_2O_{11}$ undergoes phase transitions to more ordered polymorphs, which show lower conductivity. Efforts to maintain and even, increase the ionic conductivity at low temperatures have been focused on substitution of the metal cations giving rise to a family of highly conducting electrolytes known as the BIMEVOXes (Bismuth Metal Vanadium Oxides). Examples of BIMEVOX are BICUVOX, BIZNVOX, BIFEVOX, BINOVOX, etc (that substituted with metal cation Cu, Zn, Fe, and Ni, respectivelly).

There are several methods used in the synthesis of BIMEVOXes, such as melt processing [2, 3], laser deposition [4,5], microwave synthesis [6], mechanochemical synthesis [7-10], aerosol pyrolysis [11], spray pyrolysis [12-15] and molten salt synthesis [16]. The most general method used in the synthesis of BIMEVOXes is solid-state reaction (SSR) (also called the conventional ceramic method) [17]. The SSR method involves high temperature reaction of the parent oxides or carbonates. Following the reaction, samples may be slow cooled (normal SSR) or quenched (quenched SSR). The normal SSR method results in the room temperature observation of the thermodynamically stable α, β or γ-phases depending on composition, while quenched SSR methods result in the high temperature polymorph (γ-phase). It is difficult to apply the SSR method on the industrial scale due to the high temperature used in reaction, which adds to expense and when carried out on large scales it is difficult to ensure completeness of reaction.

The Ni substituted system called BINIVOX has been synthesized using SSR methods by Abrahams *et al.* [18], Nadir and Steinfink [19], and Pernot *et al.* [20]. NiO is typically observed as an impurity [18, 19]. BINIVOX compositions of general formula $Bi_2Ni_xV_{1-x}O_{5.5-3x/2}$ display an orthorhombic structure for $x \leq 0.1$ and a tetragonal γ-phase structure for $0.1 < x \leq 0.15$ [19]. In contrast, Pernot reported that the tetragonal phase was obtained at a dopant concentration of $x = 0.07$ [20].

An alternative approach to SSR methods that minimizes the difficulty in controlling the purity of the product is the sol gel (SG) method [21-25]. In this method a solution of soluble precursor compounds is made, from which a gel is formed by addition of a suitable gelling agent. This gel is then dried and heat

treated to give the product. In this way, good contact of reactants is ensured in the reaction mixture, resulting in higher product purity. The solution nature of the process offers molecular level mixing of constituents leading to excellent chemical homogeneity and composition control, which is a particularly important feature for multicomponent systems.

Aims

The principal aim of the present project was to synthesize a range of compositions in the BINIVOX system ($Bi_2Ni_xV_{1-x}O_{5.5-3x/2}$, $x = 0.10 - 0.20$) using a SG method and to study the ionic conductivity of BINIVOX as a function of Ni concentration.

Methods

Compositions of general formula, $Bi_2Ni_xV_{1-x}O_{5.5-3x/2}$ ($x = 0.10$ to 0.20) were synthesized using a modified SG method from our previous work [26]. The starting materials were bismuth(III)nitrate ($Bi_5O(OH)_9(NO_3)_4$, Merck), ammonium metavanadate (NH_4VO_3, Sigma Aldrich, 99%), nickel nitrate ($Ni(NO_3)_2.6H_2O$, Sigma Aldrich, 99.999%), citric acid ($C_6H_8O_7$, Sigma Aldrich, 99.5+%), ethylene glycol (Merck, p.a.), distilled water, and concentrated nitric acid (Merck, p.a.). $Bi_5O(OH)_9(NO_3)_4$) solution was prepared by dissolving bismuth(III)nitrate in distilled water and to which 5 – 10 mL concentrated nitric acid (HNO_3) was added whilst stirring. The vanadium solution was prepared by diluting a mixture of NH_4VO_3 and citric acid (in a 1:10 mole ratio) using distilled water and stirring at 50 °C. The nickel solution was prepared by dissolving a stoichiometric amount of $Ni(NO_3)_3.6H_2O$ in distilled water. The clear solutions were mixed and heated to 50 °C whilst stirring until the gel was formed. The gel was then transferred to an oven and evaporated at 115 °C for 1 – 2 h. The dried gel was then placed into an alumina crucible and heated in an electric furnace at 250 °C for 12 h. After firings at 250 °C, the sample was cooled and reground. The sample was then reheated to the required firing temperature for, i.e. 450 °C for 12 h, 500 °C for 12 h, 550 °C for 12h or 600°C for 24 h, before being cooled and reground.

X-ray powder diffraction data were collected on a Philips PW1710 diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). Data were collected over the 2θ range 5 to 90° with a step width of 0.02°.

Total conductivity was measured using a Solarton 1260. The powders were pressed hydraulically to give 15 mm diameter disc shaped pellets. The thicknesses of pellets were 0.136; 0.203; and 0.0995 cm for x = 0.1; 0.15; and 0.2, respectively. Pt electrodes were painted on both sides of the pellets in 8 mm diameter which is close to 0.5 cm^2 as active area. Pt mesh of the same area was attached to the painted sides. The Pt | electrolyte | Pt assemblies were then sintered at 850 °C for 2 h with heating rate 3 °C/min and cooling rate 5 °C min^{-1}. The resistances of the cells were measured over the temperature range 250 – 750°C with a heating rate 3 °C min^{-1} in air atmosphere and frequency 0,1 – 10 MHz.

Results and discussion

The XRD results for the compositions studied were similar. Those for the $x = 0.1$ composition are shown in Figure 1 and reveal that γ-BINIVOX is obtained at 450 °C, but still contains a small amount of other phases. At 250 °C the XRD pattern reveals peaks attributable to Bi metal (JCPDS: 44-1426). At 450 °C a mixture of γ-BINIVOX and $BiVO_4$ (JCPDS:14-688) is observed. Pure γ-BINIVOX is obtained at 600 °C with an X-ray pattern similar to that previously reported [18] in the tetragonal space group $I4/mmm$.

Nguyen et al. [22] reported that BICUVOX and BICOVOX synthesized via a sol gel method using citric acid was single phase at 700 °C. However, their XRD patterns still reveal an impurity peak at around $2\theta = 27°$ typical of $BiVO_4$. These authors also reported that a crystalline phase was obtained after firing at 350 °C. Our results show that a crystalline phase is obtained after firing at 250 °C, the XRD pattern could be assigned as Bi metal. Jibo et al. [23] and Simner et al. [24] reported that BICUVOX synthesized via EDTA-citric acid and Pechini Methods was obtained as a single phase at higher temperature, 800 °C, while Hervoches et al. [25] reported that pure BICUVOX is seen after firing at 750 °C.
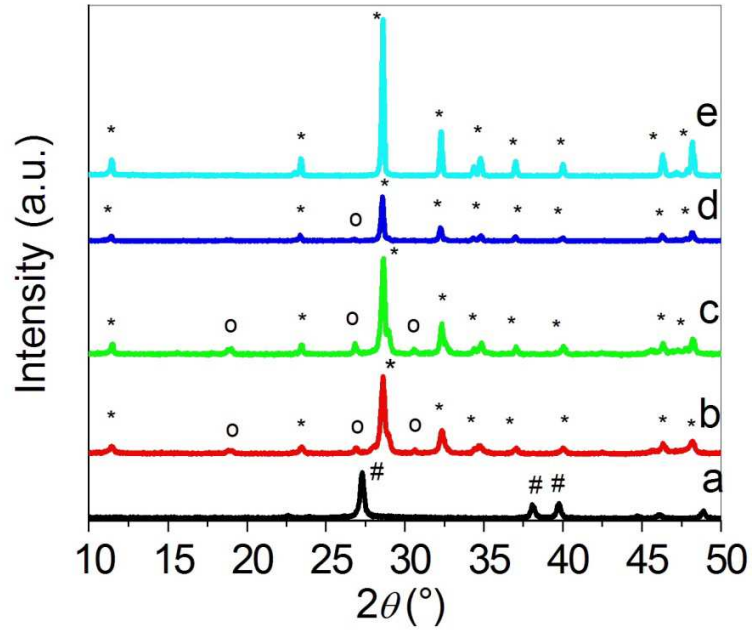
FIGURE 1. X-ray diffraction patterns of $Bi_2Ni_{0,1}V_{0,9}O_{5.5-3x/2}$ synthesized via SG after firing at (a) 250 °C 12 h, (b) 450 °C 12 h, (c) 500 °C 12 h, (d) 550 °C 12 h, and (e) 600 °C 24 h, * = γ-$Bi_2Ni_{0,1}V_{0,9}O_{5.5-3x/2}$, o = $BiVO_4$, and # = Bismuth metal. The XRD patterns for $x = 0.15$ and 0.20 are similar.

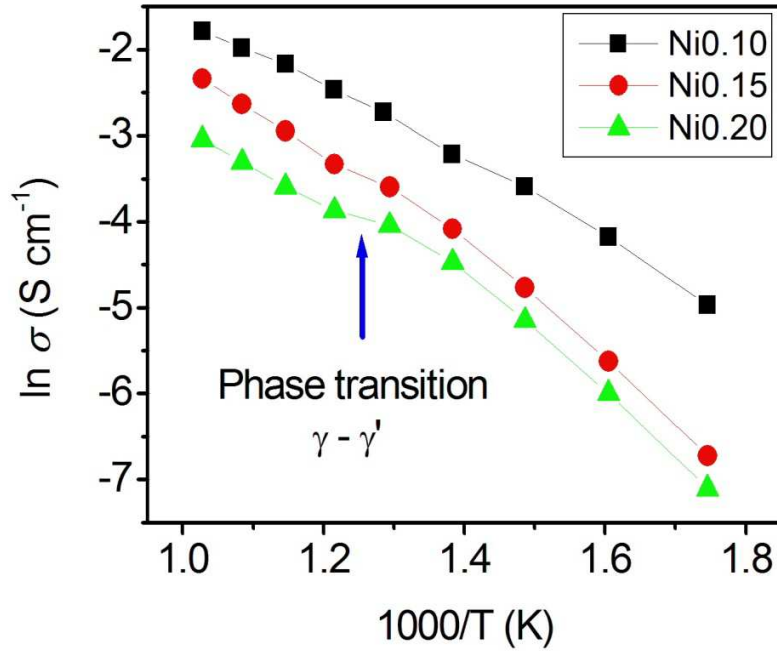**FIGURE 2.** Arrhenius plots of total conductivity for $Bi_2Ni_xV_{1-x}O_{5.5-3x/2}$.

Arrhenius plots of total conductivity for three BINIVOX compositions are shown in Figure 2. Each of the plots shows a small change in activation energy around 500°C similar to that previously reported [29], which is associated with an order disorder structure transition between the closely related γ and γ' phases. Activation energies in the low temperature region (ΔE_{LT}) are 0.41 eV, 0.60 eV, and 0.63 eV for the $x = 0.10$, 0.15, and 0.20 compositions, respectively; while in the high temperature region the respective activation energies (ΔE_{HT}) are 0.31 eV, 0.43 eV, and 0.34 eV.

Values of total conductivity at 300 °C (σ_{300}) were 6.9×10^{-3} S cm^{-1}, 1.2×10^{-3} S cm^{-1}, and 8.2×10^{-4} S cm^{-1}, for the $x = 0.10$, 0.15, and 0.20 compositions, respectively; while at 600 °C the respective conductivity values (σ_{600}) are 1.1×10^{-1} S cm^{-1}, 5.3×10^{-2} S cm^{-1}, and 2.8×10^{-2} S cm^{-1}. The values are comparable to those obtained from SSR synthesized samples [29]. At both sets of temperatures conductivity is seen to decrease with increasing Ni content. At high temperature, BINIVOX compositions exhibit conductivities roughly two orders of magnitude higher than the low temperature values, indicative of the significant disorder in the high temperature phase.

Conclusions

Single phase γ-BINIVOX was successfully synthesized at the relatively low temperature of 600°C using a sol-gel method. Ni doping of $Bi_4V_2O_{11}$ shows stabilization of the tetragonal phase between $x = 0.1$ and $x = 0.2$ as seen for SSR synthesised material, with evidence for the $\gamma' \leftrightarrow \gamma$ phase transition observed in the Arrhenius plots of total conductivity. The conductivity values show the expected decrease with increasing levels of substitution.

Acknowledgments

References

1. F. Abraham, M.F. Debreuille-Gresse, G. Mairesse, and G. Nowogrocki, *Solid State Ionics*, **28-30**, 529-532 (1988)

2. P. Kurek, J. R. Dygas, and M. W.Breiter, *J Electroanalytical Chem.*, **378**, 77-83, (1994

3. P. I. F. Paulin, M. R. Morelli, and S. C.Maestrelli, *Materials Research Innovations*, **3**, 292-296, (2000)

4. J.W. Pell, R.C.Y. Auyeung, D.B. Chrisey, and H.C. zur Loye, *Thin Solid Films*, **300**, 154-158 (1997)

5. C. Sant, and J.P. Contour, *J. Crystal Growth*, **153**, 63-67 (1995)

6. M. Gasgnier, A. Petit, M.F. Gardette, E. Rivière, S. Launay, A. Dworkin, and S. Toscani, *J. Alloys and Compounds*, **309**, 219-224 (2000)

7. P. Millán, J.M. Rojo, L. Pardo, J. Ricote, and A. Castro, *Materials Research Bulletin,* **36**, 1277-1286 (2001)

8. V. Zyryanov, *J. Structural Chem.*, **45**, S133-S141 (2004)

9. V. Zyryanov, *Inorganic Materials*, **41**, 156-163 (2005)

10. V. Zyryanov and N. Uvarov, *Inorganic Materials*, **41**, 281-287 (2005)

11. W. Guo, T.L. Ward, C. Porter, and A.K. Datye, *Materials Research Bulletin,* **40**, 1371-1387 (2005)

12. R.S. Joshi, R.K. Nimat, and S.H. Pawar, *J. Alloys and Compounds*, **471**, 461-465 (2009)

13. R.K. Nimat, C.A. Betty, and S.H. Pawar, *Applied Surface Science*, **253**, 2702-2707 (2006)

14. R.K. Nimat, R.S. Joshi, and S.H. Pawar, *Materials Science and Engineering B*, **137**, 93–98, (2007)

15. R.K. Nimat, R.S. Joshi, and S.H. Pawar, *J. Alloys and Compounds*, **466**, 341-351 (2008)

16. B. Roy and P.A. Fuierer, *J. Am. Chem. Soc.*, **92**, 520-523, (2009)

17. I. Abrahams and F. Krok, *J. Mater. Chem.*, **12**, 3351–3362 (2002)

18. I. Abrahams, J.A.G. Nelstrop, F. Krok, and W. Bogusz, *Solid State Ionics*, **110**, 95-101 (1998)

19. S. Nadir and H. Steinfink, *J. Solid State Chem.*, **143**, 9-15 (1999)

20. E. Pernot, M. Anne, M. Bacmann, P. Strobe, J. Fouletier, R.N. Vannier, G. Mairesse, F. Abraham, and G. Nowogrocki, *Solid State Ionics*, **70/71**, 259-263 (1994)

21. M.P. Peccini, USA Patent, 1967

22. H. Nguyen, P. P. Quoc, L. D. Viet, and C. H. Dang, *Advances in Technology of Materials and Materials Processing* **6**, 176-179 (2004).

23. W. Jibo, J. Baofeng, Z. Xuefeng, C. You, and Y. Weishen, *Chin. J. Catal.* **30** 926–932 (2009)

24. S. P. Simner, P.W. Wu, and B. Dunn, *J. Mater. Res.*, **13**, 866-874 (1998)

25. C.H. Hervoches, M.C. Steil, and R. Muccillo, *Solid State Sciences*, **6**, 173–177 (2004)

26. R. Rusli,, I. Abrahams, A. Patah, B. Prijamboedi, and Ismunandar, *Sintesis Oksida Bi$_2$Fe$_x$V$_{1-x}$O$_{5,5-3x/2}$ (x = 0,05–0,25) dengan Metode Sol Gel dan Reaksi Kimia Padat*, Proceedings Seminar Nasional Kimia dan Pendidikan Kimia, HKI, 2012, pp. 25-30.

27. I. Abrahams, F. Krok, M. Malys, W. Wrobel, S.C.M. Chan, W. Bogusz, and J.R. Dygas, *Solid State Ionics* **157**, 155– 161 (2003)

28. K. Shanta, G.N. Subanna, and K.B.R. Varma, *J. Solid State Chem.* 142 41 (1999)

29. F. Krok, I. Abrahams, D. Bangobango, W. Bogusz, and J.A.G. Nelstrop, *Solid State Ionics* **111** 37-43 (1998).