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Synthesis, Structure And Electrical Conductivity Of Li-Substituted $Bi_4v_2o_{11}$ Solid Electrolyte

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Abstract:

The series of compounds $Bi_{4-x}Li_xV_2O_{11-\delta}$ ($0 \le x \le 0.4$) has been prepared using solid state reaction technique. The crystal structure and conductivity were studied by using XRD and ac impedance spectroscopy. All the compounds exhibit α- type phase structure at room temperature. The β-phase appears to be suppressed for doped compounds. The conductivity of all the substituted phases is found to be higher than the parent compound. The highest conductivity ($1.02x10^{-3}$ S/cm at 420^0C) as compared to the parent compound was observed for x=0.3 substitution. The higher ionic conductivity for the doped compounds has been correlated with excess oxygen vacancies created by aliovalent substitution.

Key words: *XRD, ionic conductors, sintering, dc conductivity*

Introduction

The most commonly used electrolyte material in Solid Oxide Fuel Cell (SOFC) is yettria stabilized zirconia (YSZ) [1]. However, commercialization of SOFC with such materials is limited because of its high operating temperature. Therefore, considerable efforts have been concentrated to develop a suitable solid electrolyte which has higher ionic conductivity in the intermediate temperature range (IT; 400-800 ^{0}C). The parent compound shows three different polymorphs on heating. The α-polymorph is stable between room temperature and 430 $^\circ$C, β-polymorph between 430 ^{0}C and 570 ^{0}C and the most conductive high temperature γ-phase is stable between 570 ^{0}C up to the melting point of the compound ~870 ^{0}C. The highly pure α- $Bi_4V_2O_{11-\delta}$ phase has monoclinic structure. If the compound contains low level of impurities in the starting material, it stabilises to a closely related orthorhombic form [2].

Extensive studies have been carried out to stabilize high conducting γ-phase down to room temperature and hence optimize the ionic conductivity by partial substitution at A-site (Bi-site) and /or B-site (V-site) by iso or aliovalent metal ions [3]. This family of bismuth Vanadate has been abbreviated as BIMEVOX. The BIMEVOXes family with ME=Cu, Ni, etc. are considered as the best oxide ion conductors because below 400^{0}C, conductivities of these compounds are two orders higher than the best other oxide ion conductors [3]. So far most of the workers have concentrated their attention on substitution at B-site. On the other hand, a little work has been done on A-site substitution. Therefore, we have undertaken a systematic study to investigate the effect of partial substitution of Li at A-site (Bi-sie) on the phase transition and conductivity of $Bi_4V_2O_{11}$.

Experimental

The compounds were synthesized by solid state reaction technique. The powders of Bi_2O_3 (99%), V_2O_5 (99%) and $LiCO_3$ (99%) weighed according to formula unit $Bi_{4-x}Li_xV_2O_{11-\delta}$ ($0 \le x \le 0.4$) and thoroughly ground for 12hours in methanol environment. The mass obtained was calcined initially at 500^{0}C for 12 hours and subsequently reground and reheated at 600^{0}C for 12hours. Poly vinyl butryal was finally mixed with the powders to act as binder and pelletized by applying a pressure of ~7 tons for 1-2 minutes and the pellets were sintered at 850^{0}C for 12hours (x=0) and 675^{0}C for 12hrs (x= 0.3, 0.4) since Li-substitution considerably lowers the sintering

temperature. The x-ray diffractograms of the samples were recorded on Rigaku (Model Miniflex) using CuK_α radiation (λ= 1.54Å). Electrical measurements were performed by using a HIOKI LCR meter (model 3532-50) in the frequency range 42 Hz-5 MHz. The conducting silver paste was coated on both faces of the pellets for electrical contact. Data were collected with an input voltage 130 mV in the temperature range RT- 550°C in air.

Results And Discussion

The room temperature XRD patterns (Fig. 1) of all the samples exhibit characteristic doublets at $2\theta \approx 31^0$, 39^0, 48^0. All other reflections except a weak super lattice reflection at $2\theta \approx 24^0$ could be indexed with orthorhombic cell [4]. In addition, observation of singlets at 45.5^0 and 46.5^0 suggest orthorhombic structure. The values of the lattice parameters evaluated using 'POWD MULT' program of these compounds are listed in Table 1. The lattice parameters of undoped specimen agree well with the previous reports [4]. A gradual increase in *a* parameter accompanied by a decrease in *b* parameter, reducing their difference was observed for the doped samples. Such type of lattice parameter variations were reported earlier as the possibility of orthorhombic to tetragonal phase transition [5]. On the other hand, a sharp increase of *c* parameter results in an increase in cell volume.

The impedance plots at different temperatures are similar to those observed for other BIMEVOXes. The total resistance of the specimens at different temperatures was calculated from the point of intersection of the impedance spectrum with the real axis. The Arrhenius plots for the conductivity behaviour of solid solution $Bi_{4-x}Li_xV_2O_{11-\delta}$ with x=0, 0.3, 0.4 are shown in the Fig. 2. Unlike parent compound, which shows three regions associated with the three principal polymorphs α, β and γ, the samples with compositions x=0.3 and x=0.4 exhibit only two distinct linear regions corresponding to $\alpha \rightarrow \gamma$ transition. At relatively low temperature, the conductivity of x=0.3 composition slightly higher than the parent compound and for x=0.4 composition it is slightly less than that. Above 300^0C, the conductivity of doped compounds is more than that of undoped specimen. The composition with x = 0.3 shows highest conductivity between 300-475^0C. Above 475^0C, doped specimens have almost same conductivity; which is considerably higher than parent compound. The higher disordering of oxygen vacancies generated by aliovalent (Li) substitution and

increasing cell volume might be responsible for the significant increase in ionic conductivity of doped specimens. The activation energies (E_g) calculated by using the Arrhenius equation were found to be 0.62, 0.69 and 0.73eV corresponding to substitutions x=0, x=0.3 and x=0.4 respectively which are in the range for ionic conductor. The highest conductivity ($1.02x10^{-3}$ S/cm at 420^0C) with respect to parent compound is observed for x=0.3.

Conclusion

The influence of partial substitution of Li for Bi has been studied by XRD and dc conductivity measurements. It has been observed that the intermediate β-phase is suppressed for both x=0.3and x=0.4 substitution. The conductivities of doped specimens are found to be higher than the parent compound >300^0C and for x = 0.3 it is highest in 300-475^0C range. The enhancement of ionic conductivity of the substituted phases as compared to the host compound is explained as a result of excess oxygen vacancies generated by aliovalent substitution.

Composition	a(Å)	b(Å)	c(Å)	Volume(Å3)
x=0	5.52	5.60	15.24	471.10
x=0.3	5.55	5.57	15.33	473.91
x=0.4	5.56	5.54	15.32	471.89

Table 1: The unit cell parameters of $Bi_{4-x}Li_xV_2O_{11-\delta}$

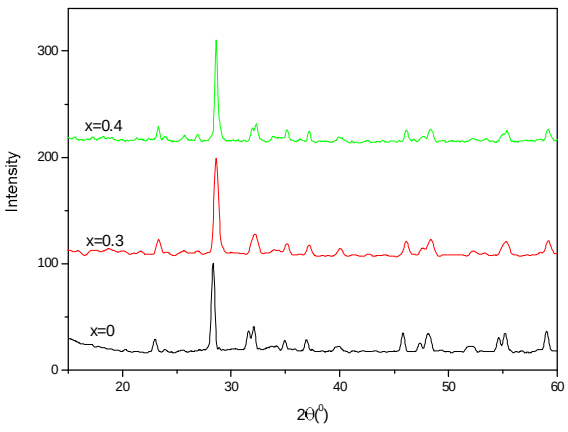

Figure 1: XRD pattern of $Bi_{4-x}Li_xV_2O_{11-\delta}$

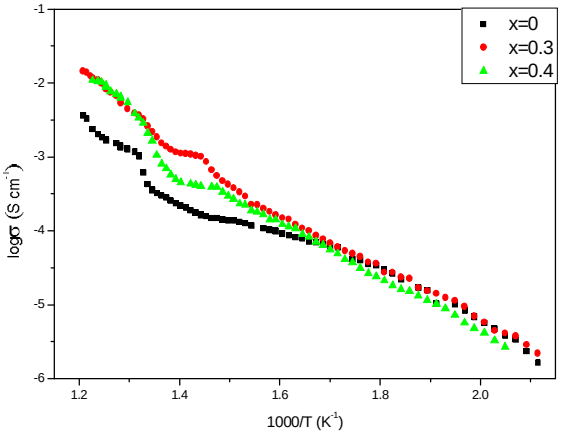

Figure 2: Arrhenius plot of $Bi_{4-x}Li_xV_2O_{11-\delta}$

Reference

1. Pirovano, C., Steil, M.C., Capoen, E., Nowogrocki, G., Vannier, R.N. (2005). Impedance study of the microstructure dependence of the electrical properties of BIMEVOXes. Solid State Ionics, 176, 2079 – 2083
2. Abrahams, I., Krok, F., Malys, M., Wrobel, W. (2005). Phase transition studies in BIMEVOX solid electrolytes using AC impedance spectroscopy. Solid State Ionics, 176, 2053 – 2058
3. Kim, S. K., Miyayama, M. (1997). Anisotropy in oxide ion conductivity of $Bi_4 V_{2-x} Co_x O_{11-\delta}$. Solid State Ionics, 104, 295–302
4. Kant, R., Singh, K., Pandey, O. P. (2010). Structural, thermal and transport properties of $Bi_4V_{2-x}Ga_x O_{11-\delta}$ ($0 \leq x \leq 0.4$). Ionics, 16, 277–282
5. Emel'yanova, Yu. V., Salimgareeva, Zh. V., Buyanova, E. S., Zhukovskii, V. M. **(**2005) Synthesis and Properties of $Bi_4V_{2-x}M_{2x}O_{11-2x}$ (M = Y, In) Solid Solutions. Inorganic Materials, 41(10), 1107–1113.