



Study on the electrical properties of Co–Ti double substituted $\text{Bi}_4\text{V}_2\text{O}_{11}$



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ABSTRACT

In the present work $\text{Bi}_2\text{V}_{0.9}\text{Co}_{0.1-x}\text{Ti}_x\text{O}_{5.35+x}$; $0.02 \leq x \leq 0.08$ was synthesized through standard solid state reaction method. X-ray diffraction and differential thermal analysis has been observed for various compositions and it was found that the tetragonal γ -phase stabilized with $\gamma' \leftrightarrow \gamma$ phase transition for all the compositions. The ionic conductivity and dielectric permittivity of BICOTIVOX have been investigated by using AC impedance spectroscopy. The values of two components of complex impedance and the relaxation time of oxide ion movement through the grain interior and grain boundary decrease with increase temperature. The thermal dependence of total ionic conductivity revealed maximum ($2.64 \times 10^{-4} \text{ S cm}^{-1}$) for $x = 0.04$ at 300°C .

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1. Introduction

Aurivillius compound with intrinsic oxygen vacancies $\text{Bi}_4\text{V}_2\text{O}_{11}$ has been introduced as solid electrolyte [1]. The bismuth vanadate $\text{Bi}_4\text{V}_2\text{O}_{11}$ characterized by two polymorphic transitions α (monoclinic) $\leftrightarrow \beta$ (orthorhombic) at 450°C and β (orthorhombic) $\leftrightarrow \gamma$ (tetragonal) at 570°C due to oxygen vacancy ordering in conducting vanadate layer [2]. The $\text{Bi}_4\text{V}_2\text{O}_{11}$ structurally showed as intergrowth of two alternating structural elements: oxygen deficient perovskite-like layers $[\text{VO}_{3.5}\square_{0.5}]^{2-}$ and fluorite-like $[\text{Bi}_2\text{O}_2]^{2+}$ layers, where \square refers to oxygen ion vacancies, which assist the conductivity where the oxide ion move through the vacancies [2]. The oxygen vacancies are disordered in the tetragonal γ -phase. The γ -phase can be stabilized above 570°C and has excellent oxide ion conductivity ($0.1\text{--}1 \text{ S cm}^{-1}$). The γ -phase of $\text{Bi}_4\text{V}_2\text{O}_{11}$ can be stabilized to ambient temperature by single or double substitution of cations for V site [3–10] to obtain good oxide ion conductors at moderate temperature [300–600 $^\circ\text{C}$].

Impedance spectroscopy is a powerful technique successfully used for the study of electrical properties of BIMEVOX, $(\text{Bi}_2\text{V}_{1-x}\text{M}_x\text{O}_{5.5-(5-n)x/2})$ where M is the substituted cation. The one advantage of AC impedance spectroscopy is to separate grain interior contribution and grain boundary contribution and electrode–electrolyte effect [11]. Nyquist diagram is used to investigate electrical properties of different microstructural regions, grain and grain boundary, of solid electrolyte.

Paydar et al. [12] reported the influence of Ti substitution on the ionic conductivity of $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{0.1}\text{O}_{5.35}$ best oxide-ion conductor

among all the BIMEVOX family ($2 \times 10^{-3} \text{ S cm}^{-1}$) and found the enhancement of ionic conductivity of BICUVOX.10. Alga et al. [13] studies the solid solution BICUCOVOX and also observed slight improvement in the oxide ion conductivity of BICUVOX.10. We have chosen Ti and Co which have high ionic conductivity of $\text{Bi}_2\text{V}_{0.9}\text{Ti}_{0.1}\text{O}_{5.45}$ and $\text{Bi}_2\text{V}_{0.9}\text{Co}_{0.1}\text{O}_{5.35}$.

In this paper, the Co–Ti doubly substituted system designated as BICOTIVOX and formulated as $\text{Bi}_2\text{V}_{0.9}\text{Co}_{0.1-x}\text{Ti}_x\text{O}_{5.35+x}$; $0.02 \leq x \leq 0.08$ has been synthesized and the electrical properties of this solid electrolyte as a function of Ti concentration has been studied.

2. Experimental

2.1. Sample synthesis

Accurate amounts of starting materials Bi_2O_3 , V_2O_5 , CoO and TiO_2 were mixed together with acetone and grinded by agate mortar for homogeneity. This paste was calcined in air at 750°C for 18 h with intermediate cooling and grinding and then mixed with acetone to obtain pure microcrystalline powder. The resulting calcined powder was isostatically pressed into pellets with same dimensions (13 mm diameter and 1 mm thickness) using Spectra-lab SL-89 at 350 MPa.

2.2. Crystallography

Compositions synthesized by standard solid state reaction were characterized at room temperature using Bruker Axs D8 with X-ray source Cu radiation ($\lambda = 1.54,060 \text{ \AA}$). The diffraction beams were collected in the range $5\text{--}70^\circ 2\theta$ with increment of 0.02° .

2.3. Differential thermal analysis

The differential thermal analysis measurements were carried out by using Perkin Elmer Thermal Analyzer. The powder was heated in nitrogen from room temperature to 750°C . The heating rate to obtain transition temperature is $10^\circ\text{C}/\text{min}$.

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2.4. Electrical measurements

Electrical conductivity measurement were carried out in air in the frequency range 20 Hz–1 MHz using Wayne Kerr LCR Meter 41,000 from temperature 150 °C to 700 °C in steps of 25 °C with 20 min stabilization time for each measurement. The pellets were sintered at 750 °C in muffle furnace for 5 h. Silver paste was coated on both the faces of pellets before heating at 650 °C for 2 h. The values of circuit parameters were estimated by non-linear least square fitting using Zview software. The characterization of surface microstructure of pellets was carried out using Scanning electron microscopy by JEOL JSM-6510LV Scanning Electron Microscopy. The chemical compositions have been investigated using EDAX analysis.

The complex impedance can be written as complex number $Z^*(\omega) = Z' + Z''$ where Z' represents the real part of impedance and Z'' represents the imaginary part of impedance. The total resistance below ~ 400 °C is equal to resistance of grain and grain boundary, $R_t = R_g + R_{gb}$, the total conductivity is calculated as $\sigma = L/(R_t A)$ where L/A is the thickness/area ratio of pellet. At higher temperature the resistance is obtained from the intercept of line inclined with real axis Z' ($R_t = Z'_{intercept}$). The total conductivity was depicted as Arrhenius plot ($\log \sigma T$ vs. $1/T$). The dielectric permittivity has been determined at constant frequency 1 MHz [14]. The dielectric constant calculated using the equation $\epsilon = (C_{1 \text{ MHz}}/\epsilon^0) \times (L/A)$ where ϵ^0 permittivity of free space (8.854×10^{-14} F/cm).

3. Result and discussion

The PXRD patterns at room temperature of various compositions calcined at 750 °C of BICOTIVOX system are shown in Fig. 1, where the influence of chemical composition variation of titanium (IV) substituted on the crystal structure of resulting calcined powder is observed. For all the compositions, the X-ray patterns showed no splitting at $2\theta \sim 32^\circ$, which reveals that the tetragonal γ -phase is stabilized due to concurrence of the doublet diffraction peak at 32° into (110) singlet diffraction peak [15,16], as also observed in the BICUTIVOX system [8].

The differential thermal analysis was carried out on the heating run from room temperature to 750 °C (illustrated in Fig. 2). The weak endothermic peaks detected for all compositions studied around 490 °C is characteristic of the tetragonal smooth changes

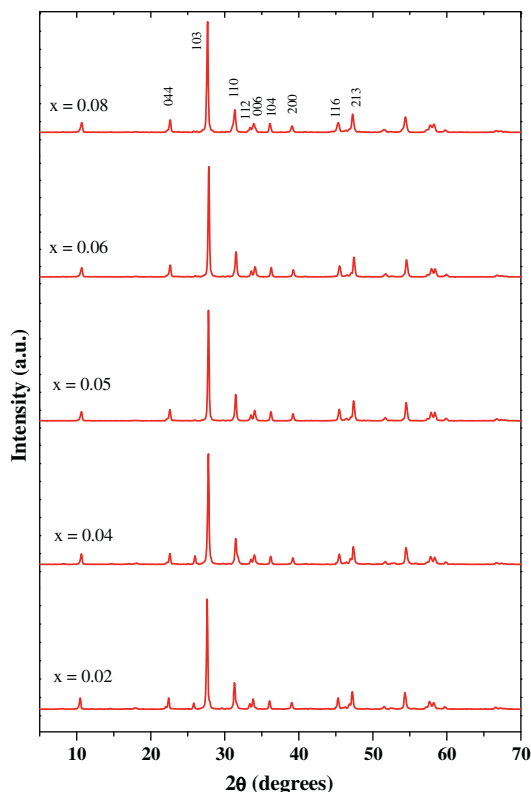


Fig. 1. XRD patterns of $\text{Bi}_2\text{V}_{0.9}\text{Co}_{0.1-x}\text{Ti}_x\text{O}_{5.35+x}$ at room temperature.

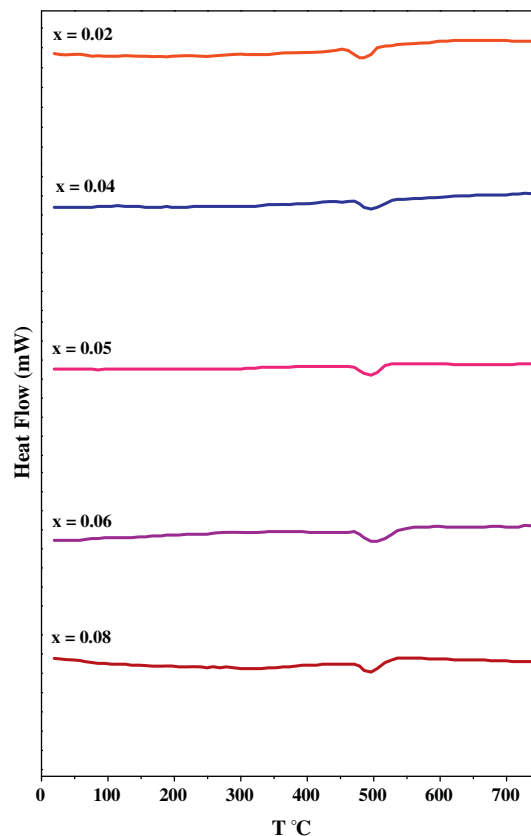


Fig. 2. DTA thermogram for BICOTIVOX as a function of composition.

of ordered γ' \rightarrow disordered γ phase transition, which is attributed to order–disorder of the oxygen vacancies in conducting vanadate layer for tetragonal phase, this small endothermic peak observe in other BIMEVOX materials [15].

Nyquist plot of the complex impedance over a wide range of frequencies for sintered pellet of the $\text{Bi}_2\text{Co}_{0.1-x}\text{Ti}_x\text{V}_{0.9}\text{O}_{5.35+x}$ system electroded by silver paste for three compositions $x = 0.02$, $x = 0.04$ and $x = 0.06$ at 150 °C, 200 °C and 250 °C has been illustrated in Fig. 3. Two semicircles are associated with presence of two electro active regions of bulk grain at high frequency and grain boundary blocking effect at lower frequency obtained below ~ 400 °C. Their separation into grain and grain boundary is associated with different relaxation time for oxide ion movement through those microstructural regions [17]. The inclined spike at lower frequency is more characteristic of the impedance of oxide ion conductor electrolyte–electrode reaction [18]; the semicircles are fitted to two parallel circuits (R_g/C_g) and (R_{gb}/C_{gb}) connected in series [6,19]. It can be noticed that as the temperature increases the diameter of these semicircles become smaller and resistance decreases (i.e., Z') and smaller diameter of semicircles arc at constant temperature observe for composition $x = 0.04$ as summarized in Table 1, which represents the values of equivalent circuit parameters obtained from the complex impedance plane plot in Fig. 3. The capacitance values of charge carrier can be calculated from the equation ($C = 1/(\omega_{top}R)$) where ω is angular frequency at the apex of semicircle, ($\omega = 2\pi f_{top}$), the capacitance values at the grain and grain boundary increase with temperature increase. The capacitance values of grain boundary around 10^{-8} F is higher than that of grain $\sim 10^{-11}$ F. The more polarization at grain boundary causes increase in the charge carrier concentration of capacitance of oxide ion at grain boundaries which increases conductivity of solid electrolyte [20]. It is interesting to note that, the ionic

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