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Synthesis and Characterization of $Bi_2Ti_xV_{1-x}O_{5.5-\delta}$ as Electrolyte Material in Solid Oxide Fuel Cell

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Abstract

Oxide materials of $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ have been synthesized by means of conventional solid state reaction method. Substitution of Ti atom for the V sites leads to the formation of single phase $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ material with I4/mmm space group of tetragonal structure as well as gives results in large grain size and good sinterability of the ceramic material. With Ti concentration of $x = 0.2$, sample without the presence of porous could be obtained. The ionic conductivity of $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ increases significantly with the presence of Ti atoms. This Ti substitution also reduces phase transition temperatures in $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ materials. The conductivity data and scanning electron microscope images show that the Ti concentration in $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ could be applied as much as $x = 0.2$, which is higher than reported before and it still gives better properties.

Keywords: *Oxide materials; Solid State Reaction; Solid Electrolyte; Ionic conductivity; Phase transition.*

1. Introduction

The need of clean energy from the renewable energy resources increases significantly in the recent years. Fuel cell is one of promising energy conversion technology that could provide clean electrical energy from renewable energy resources. Fuel cell is basically an electrochemical cell that converts the chemical energy into electricity. Hydrogen is usually used as fuel in the fuel cell and it could be obtained from the electrolysis of water or produced from ethanol using catalyst. Since it produces only water beside the electrical energy, fuel cell is widely believed as promising energy conversion device in the future.

Solid oxide fuel cell (SOFC) is one of fuel cell that uses oxide ceramics as its component. The advantages of SOFC can be mentioned here, such as, it is easy to be fabricated and handled since it consists of solid components. SOFC can also use various types of fuel such as hydrogen, CO gas and hydrocarbons that can be obtained from bioprocesses. However, the SOFC also has some disadvantages such as its operating temperature is usually high at around 1000 °C, consists of expensive materials, and its performance can be easily affected by the presence of sulfur in the fuel. In order to reduce the operational temperature, we should find cathode, electrolyte and anode materials that have good properties, high ionic and electronic conductivity at lower temperature.

Bismuth vanadate doped with metal atom ($Bi_2Me_xV_{1-x}O_{5,5-\delta}$/BIMEVOX, Me = metal atoms) is an n = 1 Aurivillius-type oxide material. Crystal structure of this material consists of perovskite blocks separated by $[Bi_2O_2]^{2+}$ layers. The high oxide ion conductivity in this material was found by Abraham *et al.*,1). However, this material goes to several phase transition below 600 °C. First, it goes from α-phase to β-phase at 450 °C and then from β-phase to γ-phase at 570 °C. The highest oxide ion conductivity was observed in γ-phase. It is interesting to have γ-phase to be stabilized at lower temperature so we could have high oxide ion conductivity at low temperature. Several attempts have been made to stabilize γ-phase at lower temperature using Cu to substitute V2-5). Other elements also have been introduced for this purpose such as Ni and Co6-7).

Substitution with Ti, however gives the highest oxide ion conductivity. Goodenough, *et al.,*8) reported that the most promising composition is one with Ti concentration of x = 0.1. However, other group reported that the highest oxide ion conductivity is found with Ti concentration of x =0.159). Here, we tried to study the optimal composition of $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ and study the detail properties of $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$. We found that the ion conductivity could be increased beyond the value as reported before and it still has good properties such as good sinterability and high ionic conductivity.

2. Experimental

For the starting materials we used oxides of Bi_2O_3, V_2O_3 and TiO_2 (all from Aldrich) with purity at least of 99.9%. These materials were weighted according to the intended compositions and mixed in the agate mortar before it was placed at furnace running at 500 °C. The first heating process was carried out for 10 hours. The initial compositions of the samples have formula of $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ with x = 0, 0.5, 0.1, 0.15 and 0.2. After first heating, samples then were ground again and pressed into pellets with diameter of 1 cm and thickness of 1 mm. Those pellets then were fired at 850 °C for 48 hours. Samples then were characterized by powder X-ray diffraction using Cu-Kα as the irradiation source for structural and phase analysis. Scanning Electron Microscope (SEM) was used to examine its morphology and LCR-meter was used to measure its complex impedance or conductivity.

3. Results and Discussion

The results from the X-ray powder diffraction measurement are shown in Figure 1. In the BIMEVOX sample that was not substituted with Ti, we could observe many reflectance peaks. The diffraction pattern does not show the characteristic pattern of bismuth vanadate materials in the γ-phase. The diffraction pattern of $Bi_2VO_{5,5-\delta}$ indicates that the undoped bismuth vanadate is formed in different crystal structure with different space group. By substitution of small amount of Ti, the diffraction pattern change dramatically and show the diffraction pattern of bismuth vanadate compound in the γ-phase as it will be confirmed by structural refinement. We could see that with x = 0.2, we could obtain almost single phase BIMEVOX materials.

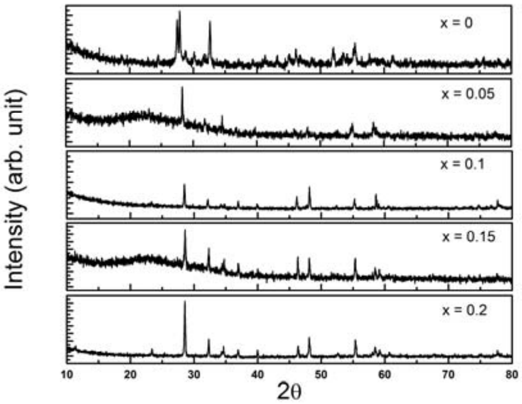

Figure 1. Diffraction pattern of $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ materials with x = 0.0, 0.05, 0.01, 0.015, 0.2 prepared by solid state reaction.

In order to determined the crystal structure and crystal parameters, we carried out refinement on the X-ray diffraction pattern of $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ with tetragonal structure and I4/mmm space group[10]. Refinements processes were carried out using Le Bail method implemented in the Rietica program. The residual parameters of R_p and R_{wp} were found to be below 10 % for the Ti doped samples indicating that the refinement results could be accepted or the samples actually have tetragonal structure with I4/mmm space group. The lattice parameters for $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ were plotted against Ti concentration in Figure 2. The lattice parameter, a is decreasing rapidly from x = 0.05 to x = 0.1 then it increases slightly. Meanwhile, the c value decreases up to x = 0.15 and then increases. The ionic radius of Ti^{4+} (60 pm) is slightly larger than V^{5+} (54 pm)[11]. Therefore, the lattice parameters are expected to increases. However, we observed the decreasing of lattice parameters and we could attribute the decreasing in the lattice parameters is caused by the increasing of oxygen vacancies. The increasing of oxygen vacancies will cause some of the metal ions will have lower coordination number and will change their local structure from the octahedral to the tetrahedral coordination. This will give distortion of the oxygen positions and cause the decreasing of lattice parameters. Meanwhile, the increasing of oxygen vacancies is caused by the substitution of Ti (with oxidation number of 4+) that replaces V (with oxidation number of 5+). Lower oxidation number of Ti would lead to the reduction of oxygen content since it needs less oxygen to balance the charge in the crystal.

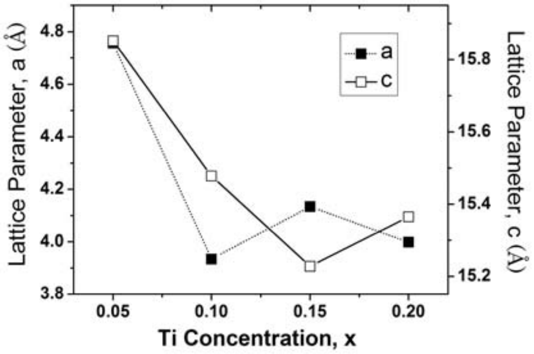

Figure 2. Lattice parameter of tetragonal $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ materials with x = 0.05, 0.01, 0.015, 0.2 prepared by solid state reaction Å.

The SEM images of the $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ material are shown in Figure 3. The image of $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ without Ti substitution shows that the material consists of small and rounded grains. It is also clear that there is no connection between grains. These conditions are not favorable for application as electrolyte material in solid oxide fuel cells, since it will give low ionic conductivity. Very different morphology is observed in the samples that were substituted with Ti. First, it forms large grains but we still could observe the presence of porous. The presence of porous or voids in the material is not accepted for application as electrolyte material in the SOFC. The electrolyte of the SOFC should have high density with no porosity so they could block the gas exchange from cathode to anode or vice versa. In the sample with Ti concentration of 0.2, the grains became large with very small area of voids. This morphology is considered to suitable for the electrolyte materials. The average of grain diameter in this sample is around 50 µm.

The ionic conductivities of $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ were measured using LCR-meter. From the impedance data, we calculated the real and imaginary part of conductivity. The measurements were carried out from 600 °C to around 150 °C. Here in this paper, we show the data that we obtained from temperature of 250 °C and 300 °C as examples in Figure 4. Other impedance data had similar pattern but with different values.

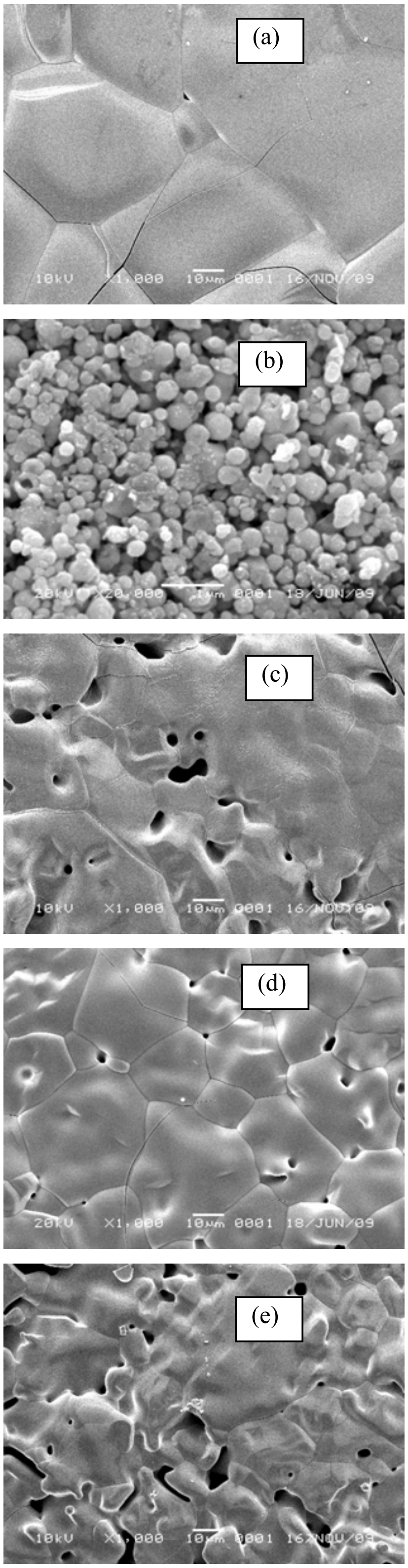

Figure 3. Scanning electron microscope images of $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ materials with x = 0.0, 0.05, 0.01, 0.015, 0.2 prepared by solid state reaction.

We could see that there are two separated semicircles. The left semicircle indicates the ionic conductivity in the grain and on the right; it comes from the inter-grain conductivity. We could not determine the exact value of the inter-grain conductivity. However, we could determine the ionic conductivity within grains. This conductivity is more important in order to determine the phase transition in $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$. In all samples, as temperature decreases we could see large increment in the impedance value as the semicircle enlarges. With the increasing of Ti concentration, the impedance also decreases. We could estimate that the grain impedance of sample with Ti of 0.05 at 250 ^{o}C is around 460 kΩ. Meanwhile, for sample with Ti concentration of 0.2 at the same temperature, the real impedance is around 55 kΩ. This indicates that the conductivity of sample still could be increased beyond Ti concentration of 0.15.

The conductivity data obtained from the previous data were analyzed further by plotting the conductivity data against temperature. The results are given in Figure 5. In the Arrhenius plot, we could see that the overall ionic conductivity increases as the Ti concentration increases. In our case it seems that the conductivity could be increased beyond the Ti concentration of 0.2. We found that at low Ti concentration the conductivity data (ln σ) are not linear against the inverse temperature. This indicates that the $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ goes to several phase transitions. First, it has transition at around 300 ^{o}C and second at around 500 ^{o}C for sample with $x \neq 0$. These are transition temperatures from α phase to β phase and β phase to γ phase, respectively. We could determine the transition temperature from these conductivity data by determining the conductivity slope. Different slope in the curves could be from the different phases and the intersection between two slopes could be estimated as the transition temperature. The transition temperature data against Ti concentration are plotted in Figure 6. It is clearly observed that the rapid decreasing of the transition temperature could be observed in the sample with Ti concentration up to x = 0.05. Slower decreasing in the transition temperature is observed in the higher Ti concentration. These transition temperatures are lower compared to the transition temperature as reported before$^{1)}$. Therefore, substitution of Ti atoms at the vanadium sites could reduce the transition temperature and Ti concentration still could be increased up to x = 0.2. We found that the transition is not noticeable at higher Ti concentration. The conductivity data in the Arrhenius plot for sample with x = 0.2 are almost linear at wider temperature range. There is a probability that we have a transition temperature at around 300 ^{o}C. However, we must confirm the exact phases that related with this transition by other measurements, such as temperature dependence of X-ray diffraction.

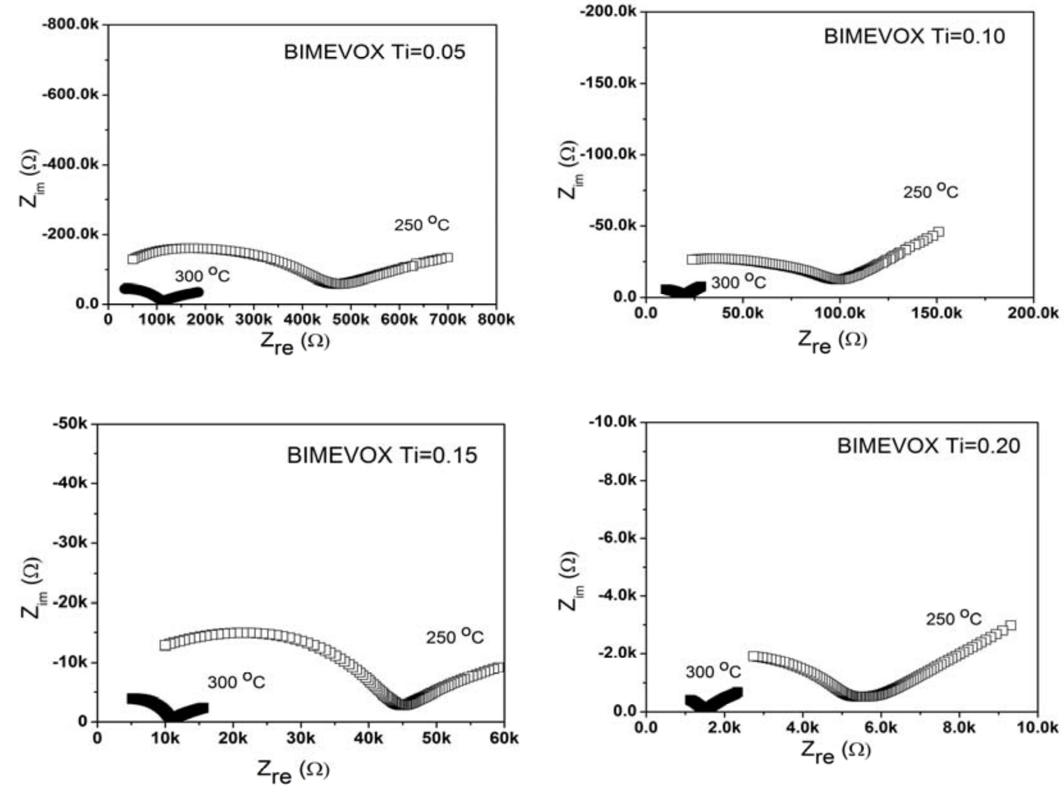

Figure 4. Plot of complex impedance of $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ materials with x = 0.05, 0.01, 0.015, 0.2 prepared by solid state reaction measured at 250 and 300 °C.

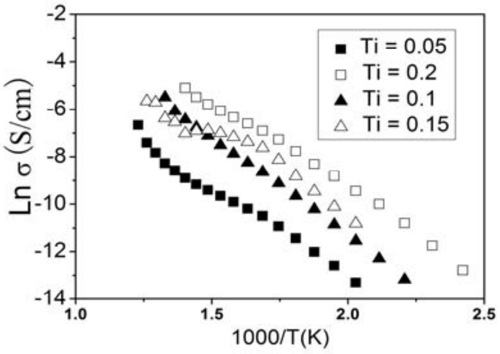

Figure 5. Arrhenius plot of ionic conductivity of $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ materials with x = 0.05, 0.01, 0.015, 0.2 against inverse temperature.

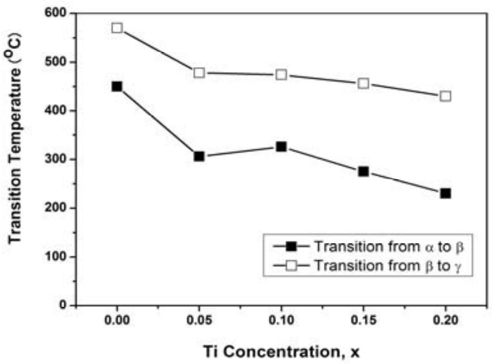

Figure 6. Transition temperatures from the α to β-phase and from the β to γ phase in $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ materials with Ti concentration of x = 0, 0.05, 0.01, 0.015, 0.2.

4. Summary

$Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ materials with different Ti concentration have been synthesized by means of solid state reaction technique and characterized using X-ray diffraction technique, scanning electron microscope and impedance measurement at different temperatures. Substitution of Ti into the vanadium sites increases the crystallinity of $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$ material and also increases the ionic conductivity. It was found also that the substitution with Ti reduces the transition temperature in the $Bi_2Ti_xV_{1-x}O_{5,5-\delta}$. The Ti concentration with x = 0.2 still could reduce the transition temperatures in the BIMEVOX materials.

Acknowledgement

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