Modeling Ionic Conduction in γ-Bi$_2$VO$_{5.5}$

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Abstract-γ-Bi$_2$VO$_{5.5}$ family oxides has potential to play important role in solid oxide fuel cell, especially as the electrolyte due to their high ionic conductivity. In this work, oxide conduction in γ-Bi$_2$VO$_{5.5}$ is modeled based on bond valence sum (BVS) method. In γ-Bi$_2$VO$_{5.5}$, there are oxide vacancies at the equatorial position in the perovskite-like layers. These vacancies can facilitate oxide movement. The γ-Bi$_2$VO$_{5.5}$ model was built in a primitive structure with the entire V coordination in one layer are tetrahedron and entire V coordination in the next layer are octahedron. Oxygen movement, based on BVS result, mainly occurs in equatorial site i.e. on [140] direction. The minimum achieved BVS value was 1.320, which is considered as a site that has large cavity and facilitates oxygen hopping.
Keyword: γ-Bi$_2$VO$_{5.5}$, BVS, oxygen conduction.

I. INTRODUCTION

Solid electrolyte materials with high oxide ion conductivity at low temperature are intensively investigated in order to have solid oxide fuel cell (SOFC) capable of operating at low temperature. One of oxide material that has high oxide ion conductivity is γ-Bi$_2$VO$_{5.5}$. As comparison to the materials widely used as a solid electrolyte material, such as yttria stabilized zirconia (YSZ), γ-Bi$_2$VO$_{5.5}$ has ionic conductivity of 1×10^{-2} Scm^{-1}, which is around three orders of magnitude larger than YSZ at same temperature of 300 °C [1]. Therefore γ-Bi$_2$VO$_{5.5}$ has potential application as electrolyte in SOFC working at low temperature.

The structure of Bi$_2$VO$_{5.5}$ can be derived from Bi$_2$WO$_6$ and γ-Bi$_2$MoO$_6$ by formation of oxide vacancies in the metal oxide layers; thus the compound can be formulated (Bi$_2$O$_2$)(VO$_{3.5}$ $_{0.5}$), where is the corresponding to intrinsic oxide vacancy [1, 2]. The Bi$_2$VO$_{5.5}$ goes to several structural transformations and known has several polymorphs but essentially, there are only three main polymorphs, namely α, β, and γ with the transformations: $\alpha \rightarrow \beta$ at 447 °C and $\beta \rightarrow \gamma$ at 567 °C. The structures of α and β-phases are more ordered, larger in unit cell, and have lower conductivity. At the high temperature, γ-phase is formed and has maximum conductivity of 0.2 Scm^{-1} at 670 °C [3].

Experimental studies on the oxide conductivity of γ-Bi$_2$VO$_{5.5}$ have been reported elsewhere [4]. However, the experimental study could not reveal the detail of the mechanism of ionic conduction. Abraham and Krok proposed oxide conduction mechanism which was applied only to BIMEVOX with ME is divalent metal, and derived from crystallographic data [5]. In

our knowledge, the conduction mechanism in parent structure of BIMEVOX, γ-Bi$_2$VO$_{5.5}$, has not been reported yet. Computational studies could be used to study the detail of ionic conductivity mechanism in the atomic level. Some computation study on the layered structure of Aurivillius phases similar to γ-Bi$_2$VO$_{5.5}$ has been carried out and reported [6]. It could reveal defect energies and maximum dopant concentrations in Aurivillius as ferroelectric material.

Here, we report the computational study of γ-Bi$_2$VO$_{5.5}$ structure that cover trajectory of oxide in γ-Bi$_2$VO$_{5.5}$. The study was aimed to investigate the oxide pathways that are possible in the γ-Bi$_2$VO$_{5.5}$ structure via vacancy defect in perovskite-like layer.

II. EXPERIMENTAL METHOD

In this study, oxide migration in γ-Bi$_2$VO$_{5.5}$ is calculated using by method of bond valence sum (BVS). BVS method is empirical model which predict oxidation state based on distances with neighbor atoms. The rule of bond valence is formulated:

$$V_i = \sum S_{ij} \qquad (1)$$

The equation above shows the empirical relationship between bond valence and bond length or the distance between ions i and j (R_{ij}) which is defined:

$$V_{ij} = \exp\left(\frac{R_0 - R_{ij}}{b}\right) \qquad (2)$$

where R_0 is a constant and b is universal constant which is 0.173. In this work, the value of R_0 and b are 0.516 Å and 1.171 Å, respectively.

The method has been successfully used to model the movement of cations in solid materials, such as Na$^+$ in the NASICON (sodium super ionic conductor) and K$^+$ in KFeAs$_2$O$_7$ [7, 8]. In this study, movement or geometry conduction for oxide in γ-Bi$_2$VO$_{5.5}$ structure is predicted by using the BVS method as has been performed by JUMPITER [9].

γ-Bi$_2$VO$_{5.5}$ structure which is built in this work are an simple model that can represent the structure, especially by paying attention the possibility of various vanadium coordination environment in the perovskite-like layer. Here, we built model of γ-Bi$_2$VO$_{5.5}$ as simple as possible to get insight the oxide conduction of γ-Bi$_2$VO$_{5.5}$. This model is a primitive structure for one unit cell of γ-Bi$_2$VO$_{5.5}$ where perovskite-like layers

have two different vanadium coordinations, namely tetrahedron and octahedron. In the middle the layer, V coordinations are entire tetrahedron, meanwhile, the upper and lower perovskite-like layers of γ-Bi$_2$VO$_{5.5}$ have entirely octahedral coordination.

III. RESULT AND DISCUSSION

Structures of model were created based on γ-Bi$_2$VO$_{5.5}$ structure reported by Mairesse *et al*. as depicted in Figure1. [10]. The γ-Bi$_2$VO$_{5.5}$ is tetragonal with space group is $I4$/mmm, and cell unit dimension is $a = 3.99176(4)$, $b = 3.99176(4)$, and $c = 15.4309(3)$ Å. The structure has high symmetry and contains oxygen vacancy in perovskite-like layer. Environment of the V^{5+} coordinations in perovskite-like layer are recognized as octahedron, tetrahedron, trigonal bipyramid, and tetragonal pyramid with interatomic distances compatible with O atomic size. Based on the vanadium coordination environment, we built a model structure of γ-Bi$_2$VO$_{5.5}$with $P1$ space group by creating oxide vacancies at the equatorial site, so the perovskite-like layer becomes entire tetrahedrons, and other layers were octahedron (Figure 2). The structure is far from the real structure of γ-Bi$_2$VO$_{5.5}$, however we expect that an insight of the role of non octahedron coordination in the oxide conduction could be obtained.

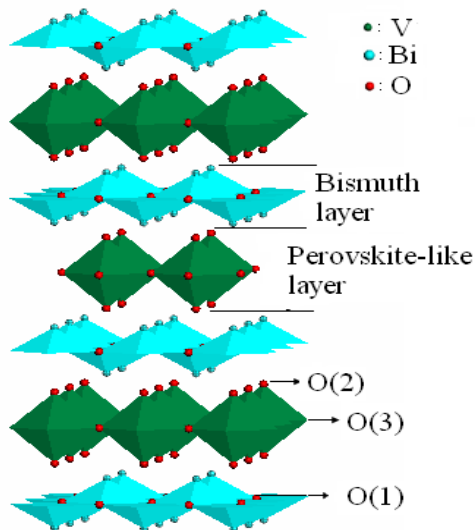Figure 1. The refined crystal structures of γ-Bi$_2$VO$_{5.5}$; vacancies in perovskite-like layers were not shown. O(3) and O(2) each are equatorial and apical oxides, respectively.

III.1 Trajectory of Oxide Conduction in γ-Bi$_2$VO$_{5.5}$

To find a most possible the pathway in the γ-Bi$_2$VO$_{5.5}$ structure, we do the calculations using by the bond valence sum. As a preliminary step, the structure of γ-Bi$_2$VO$_{5.5}$ is optimized. Geometry optimization of model carried out by Density Functional Theory (DFT) method using by the CASTEP program.

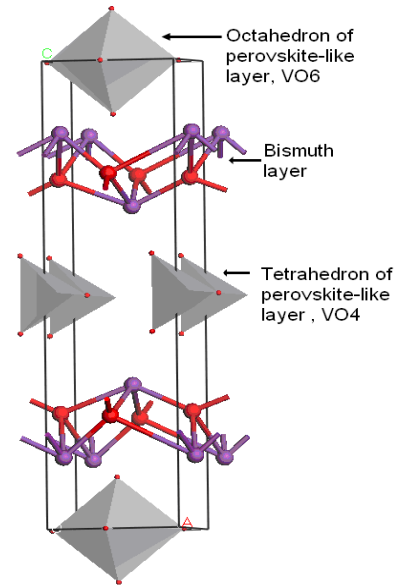Figure 2. Model of γ-Bi$_2$VO$_{5.5}$ structures; vacancies in equatorial site of perovskite-like layers (tetrahedron coordinations, VO$_4$) were not shown. The other coordinations of parovskite-like layers (upper and below) are octahedron, VO$_6$.

The activation energy of oxide to move to vacant position is calculated using by *ab initio* method. The results showed that oxide ion migration into vacant positions in the perovskite-like layer requires activation energy of 0.38 eV. This result is in a good agreement to experimental results [4, 11-13], although, Joubert *et al*. reported a value of 0.19 eV [14]. Based on the activation energy result, the structure is a good model for *ab initio* methods as well as bond valence sum, but not for molecular dynamic.

The oxide conduction was very difficult as indicated by maximum BVS value was very high, reaching twice the valence of oxygen. On the upper and lower perovskite-like layers of γ-Bi$_2$VO$_{5.5}$ are entirely octahedral coordination, thus hopping oxygen is not possible since there is no vacancy.

Pathway of oxide in the structure was modeled by using the JUMPITER software based on bond valence sum on various directions. Oxide movements into the apical site reached potential barrier very quickly with BVS of 11.758 at 0.131 Å distance. Therefore, oxide movement was calculated in equatorial site, that could be modeled on the directions of [100], [010], and [ab0]. Bond valence sum of trajectory O(3) in the these directions is shown in Figure 3. It could be seen that the movement of oxide are difficult into the directions of a and b. The covered oxide migration distances in [100] and [010] directions do not exceed 1.2 and 0.4 Å, respectively. The easy conduction path of ionic conductivity in the γ-Bi$_2$VO$_{5.5}$ is in the direction of ab, as given in the Figure 4.
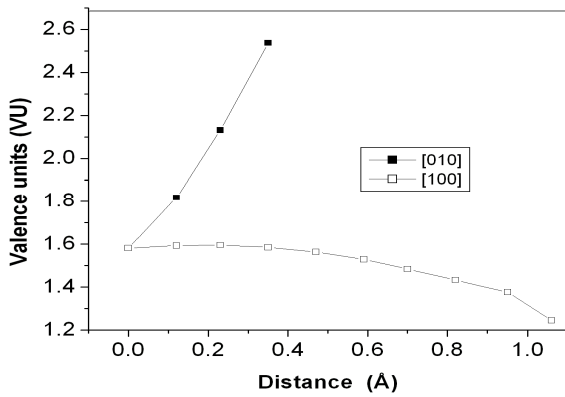
Figure 3. BVS of oxide on [100] and [010] directions in the perovskite-like layer of γ-Bi$_2$VO$_{5.5}$. Distances of oxide migration in [100] and [010] directions do not exceed 1.2 and 0.4 Å, respectively.
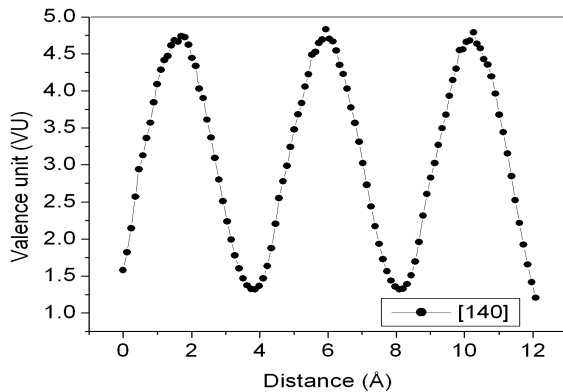

Figure 4. BVS of oxide on [140] direction in the perovskite-like layer of γ-Bi$_2$VO$_{5.5}$. Hopping distance of oxide is 3.86 Å.
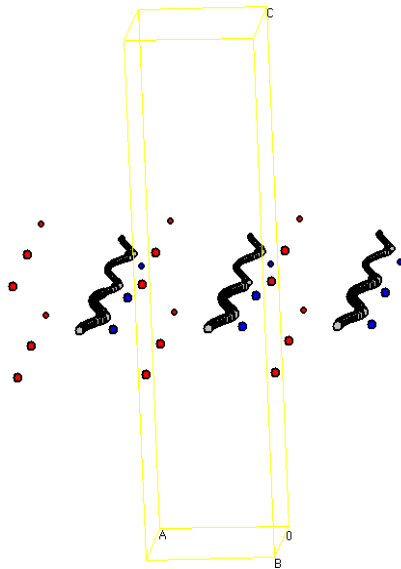

Figure 5. Pathway of oxide in equatorial site of perovskite-like layer. The pathway take places in tetrahedron coordination, with distance hopping oxide is 3.86 Å from O(3) to (O3) vacant.

In this model, oxygen ions are easier to move in [140] direction, which connect the O(3) with other O(3) with a hopping distance of 3.86 Å. Along these pathways the maximum value of BVS is 4.472, and the minimum value is 1.320, i.e. within range of +223% to 66% from ideal value of 2. Querfelli *et al.* reported BVS of K$^+$ cation in KFeAs$_2$O$_7$ structure were within +197% (max BVS = 1.97) maximum and 89% (min BVS = 0.89) minimum [8]. Mazza reported that the maximum and minimum BVSes of Na$^+$ cation were 1.4 and minimum 0.42, i.e. within range of 140 and 42% [7]. Thus, it could be seen that the range BVS values along the pathway are similar to those of other ion conductors. Oxygen ion migration parallel to *ab* plane is in agreement with that was proposed by Abraham and Krok [5], where a suitable pathway is available through vacant sites located in equatorial vanadate plane between four vanadium polyhedrals. The vacant site of vanadate layer is faced directly and coordinated linear to Bi 6s^2 lone pair orbital of (Bi$_2$O$_2$)$^{2+}$ layer. Interaction between layers of (Bi$_2$O$_2$)$^{2+}$ and vanadate in γ-Bi$_2$VO$_{5.5}$ is ionic. In this site, transient oxide ions can endure electrostatic repulsion, and due to well polarizability of the Bi 6s^2 lone pair orbital, so this route in equatorial site can avoid oxygen ions more close to vanadium ions [5].

This study suggests that the oxide is easier to migrate between equatorial site rather than from equatorial to apical or vice versa. The more realistic model of course is model with various coordinations in perovskite-like layers, namely tetrahedron, five-coordination, and octahedron. The result of ionic conductivity calculation in these models will be reported.

IV. CONCLUSION

Computational simulation of ionic conductivity of γ-Bi$_2$VO$_{5.5}$ has been performed using BVS method. Pathways of oxide conduction are within equatorial site on coordination environment of V-O. Oxide ions are easier to move on the [140] direction which is parallel to *ab* plane in perovkite-like layers, with minimum BVS of 1.320.

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