First-principles study on oxygen ion conduction of La$_2$GeO$_5$ based on the density functional theory

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Abstract. We performed first-principles simulations based on the density functional theory for investigations on the atomic geometry of La$_2$GeO$_5$, which is a fast oxygen ion conductor applicable to solid oxide fuel cells. While two experimental studies have reported contradicting results about the configuration of GeO$_4$ tetrahedral substructures, i.e., sp$^2$- or sp$^3$-like, we found that only the sp$^3$-like form is stable. We confirmed that the favorability of oxygen sites for vacancy formation is fundamentally affected by this configuration. The bonding mechanisms between atoms are discussed based on analyses of atomic distances and electronic density of states.

1. Introduction
Development of rechargeable batteries with high energy densities, high capacities and long lifetimes has become an urgent issue for realizing a low-carbon economy based on technologies for stable electricity supplies by renewable energy resources, effective leveling of electric power loads, and replacement of fossil fuel-powered vehicles with electric vehicles. Currently, lithium-ion batteries and lithium-ion polymer batteries have become common commercial products with high energy densities; however, their capacities are still insufficient to meet the demands of a low-carbon economy. Moreover, the use of lithium makes the batteries unstable and unsafe at the high temperatures reachable during practical operation.

One promising replacement is use of solid oxide fuel cells (SOFCs) designed as metal-air rechargeable batteries. The electrolyte membranes and electrodes of SOFCs consist of oxygen ion conductors, which transmit O$^{2-}$ ions between the air and fuel electrodes. In the discharging process, oxygen molecules are dissociated into O$^{2-}$ at the air electrode by cathode reactions, diffuse through the membrane toward the fuel electrode due to the concentration gradient, and finally react by anode reactions with the fuel contained in the storage container connected to the fuel electrode. In contrast, in the charging process, O$^{2-}$ ions are produced from the oxidized fuels in the storage container by cathode reactions at the fuel electrode, diffuse through the membrane toward the air electrode due to the concentration gradient and electrochemical potential gradient, and finally form oxygen molecules at the air electrode by anode reactions. SOFCs are stable, safe and less affected by the atmosphere even at high temperatures of around 1300 K because the devices are ceramic-based and the reactions of fuels...
However, modification of this hypothesis has become necessary due to the discovery that La\(_2\)GeO\(_4\) takes place in the inner part of the devices. Thus, SOFCs can realize high energy densities safely in high temperature ranges for which the carrier mobility is high.

So far, various ceramic materials based on or containing rare-earth elements have been studied as oxygen ion conductors\cite{1}. Yttria-stabilized zirconia and ceria-based ceramics are representative conventional materials for SOFCs. The operating temperatures of SOFCs realized by these materials are approximately in the range from 1073 to 1273 K, which is still extremely high for practical applications in which the lower limit needs to be about 500 K. Therefore, it is crucial to develop new oxygen ion conductors that have higher ionic conductivities at low temperatures.

The mechanisms that determine the oxygen ion conductivity are not understood yet. It had been believed that a high isotropy of the crystal structure gives rise to high ionic conductivity, as for the case of the discovery of LaGaO\(_3\) with a pseudocubic perovskite lattice as a fast oxygen ion conductor \cite{2–5}. However, modification of this hypothesis has become necessary due to the discovery that La\(_2\)GeO\(_4\) with a highly anisotropic monoclinic lattice also has a high ionic conductivity over a wide range of oxygen partial pressure \cite{6–8}.

Usually, oxygen ion conduction takes place by migration of lattice defects, which can be classified as either interstitial oxygen atoms or oxygen vacancies; for example, LaGaO\(_3\) and La\(_2\)GeO\(_3\) belong to the latter category. In oxygen-deficient materials where vacancy propagation accounts for the conduction, identification of oxygen-rich layers that contribute to the conduction is an important subject for clarification of the conduction mechanisms.

The atomic geometry of stoichiometric La\(_2\)GeO\(_5\) was first studied by Ishihara \textit{et al.} using the X-ray diffraction method with Rietveld analysis, and was reported to be characterized by distorted GeO\(_4\) tetrahedral substructures \cite{6}. It was also found that the atomic coordination is preserved in nonstoichiometric La\(_{2-x}\)GeO\(_{5-\delta}\) for \(x < 0.33\) \cite{6} while the monoclinic lattice is preserved for \(x < 0.45\). This results in two types of well-defined planar layers, i.e., LaGeO\(_3\) and LaO\(_2\). According to the atomic distances, three atoms in the LaGeO\(_3\) layers are coordinated around a germanium atom in the configuration of sp\(^2\) hybridization. On the other hand, Berastegui \textit{et al.}, who also performed X-ray diffraction measurements, reported that the GeO\(_4\) tetrahedral substructures in the stoichiometric La\(_2\)GeO\(_5\) become rather symmetric by undergoing sp\(^3\)-like Ge-O coordination \cite{8}. They also found that the lattice structure changes to a hexagonal apatite-type structure for a nonstoichiometric composition of \(x = 0.45\), which leads to higher oxygen ion conductivities than the monoclinic case. Thus, before discussing the conduction mechanisms, it is necessary to resolve this experimental contradiction regarding the atomic geometry. However, no theoretical study on the stable geometries of monoclinic La\(_2\)GeO\(_5\)-based materials has been reported yet.

In this paper, we investigate the stable atomic geometry of stoichiometric La\(_2\)GeO\(_5\) with a monoclinic lattice by first-principles calculations based on the density functional theory (DFT). We also carry out an analysis of the favorable sites for oxygen vacancy formation based on total energy calculations. The bonding properties between atoms are discussed with the aid of an analysis of the electronic density of states.

2. Computational methodology

The calculations were performed using the Vienna Ab-initio Simulation Package (VASP) code. We employed the generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) functional for the exchange-correlation energy. The interactions between ions and electrons were given by the projector augmented-wave (PAW) method. The total energy convergence was confirmed with a cut-off energy of 900 eV and k-point sampling by the Monkhorst-Pack scheme with a \(3 \times 3 \times 3\) mesh. It should be noted that the required cut-off energy was much higher than the usually expected value, which is about 550 eV for treatment of the target composition with standard PAW potentials of VASP. The tetrahedron method with Blöchl corrections is employed for total energy calculations.

We employed a monoclinic unit cell containing 32 atoms as the initial structure according to the experimentally obtained data \cite{6, 8} as shown in Table 1. The differences in the volumes and lattice
Table 1. Atomic coordinates of La$_2$GeO$_5$ in the initial geometries with the $P2_1/c$ space group given in fractional coordinates for each corresponding lattice with $a = 9.59693$ Å, $b = 7.47359$ Å, $c = 7.10745$ Å and $\beta = 107.5770^\circ$ (485.971 Å$^3$ volume) for the sp$^2$-based structure [6] and $a = 9.60405$ Å, $b = 7.46902$ Å, $c = 7.11199$ Å and $\beta = 107.550^\circ$ (486.417 Å$^3$ volume) for the sp$^3$-based one [8].

| Site | X    | Y    | Z    | X    | Y    | Z    |
|------|------|------|------|------|------|------|
| La(1) | 0.38937 | 0.14161 | 0.57941 | 0.38289 | 0.14396 | 0.58432 |
| La(2) | 0.02056 | 0.12360 | 0.72966 | 0.02148 | 0.12451 | 0.73529 |
| Ge   | 0.29732 | 0.58935 | 0.53976 | 0.29880 | 0.58817 | 0.54080 |
| O(1) | 0.32250 | 0.06691 | 0.86216 | 0.2919 | 0.0748 | 0.8573 |
| O(2) | 0.34794 | 0.48623 | 0.75895 | 0.3695 | 0.4558 | 0.7496 |
| O(3) | 0.35157 | 0.77243 | 0.49523 | 0.4074 | 0.7723 | 0.5523 |
| O(4) | 0.04677 | 0.61215 | 0.49451 | 0.1117 | 0.6371 | 0.4917 |
| O(5) | 0.04310 | 0.12912 | 0.45330 | 0.1140 | 0.1217 | 0.4493 |

Figure 1. Initial geometries of La$_2$GeO$_5$ for (a) the sp$^2$-based structure and (b) the sp$^3$-based structure in an expanded cell with $2 \times 2 \times 2$ periods. Green, gray and red balls denote lanthanum, germanium and oxygen atoms, respectively. Arrows indicate $a$, $b$ and $c$ axes, respectively. Magenta lines indicate GeO$_4$ tetrahedral substructures.

The Ge-O(1), Ge-O(2) and Ge-O(3) distances in the sp$^2$-based structure are 1.79, 1.67 and 1.53 Å, respectively. Thus, the Ge-O(1) and Ge-O(2) distances are similar to that for a single bond (1.73 Å) and the Ge-O(3) distance is similar to that for a double bond (1.57 Å), according to Pauling’s definition. The Ge-O(4) distance is 2.33 Å and is significantly longer than the covalent bond length. Here, the parameter between the two structures are within 1 %. The corresponding geometries are shown in Figure 1. While the oxygen positions are quite different between the two structures, the positions of lanthanum and germanium are almost equivalent with each other. In both structures, La(1), Ge, O(1), O(2) and O(3) form LaGeO$_3$ layers and La(2), O(4), O(5) form LaO$_2$ layers. The GeO$_4$ tetrahedral substructures consist of Ge, O(1), O(2), O(3) and O(4). It is seen that the LaO$_2$ layers are well-defined in the sp$^2$-based structure while they are spread in the sp$^3$-based one.
La(2)-O(4) (2.24 Å) and La(2)-O(5) (2.04 Å) distances are somewhat shorter. Both the La(2)-O(4) and La(2)-O(5) distances are shorter than the La-O single bond length, 2.24 Å, defined in the same way as Ge-O. The O(4)-O(5) distance is 2.19 Å and is therefore considered to be non-interacting. On the other hand, the Ge-O(1), Ge-O(2), Ge-O(3) and Ge-O(4) distances in the sp\(^3\)-based structure are 1.77, 1.74, 1.71 and 1.76 Å, respectively, all of which are similar to the single bond length. Here, the La(2)-O(4), La(2)-O(5) and O(4)-O(5) distances are 2.48, 2.40 and 2.94 Å, respectively, and therefore longer than the covalent bond length.

The lattice parameters and atomic positions were relaxed by the conjugate-gradient algorithm with a force scaling constant of 0.5 fs until the total energy convergence reached less than 0.01 meV. The relaxation calculations were executed in two steps by initializing the electronic basis set after the first convergence in order to reduce the Pulay stress. Then, the optimized electronic properties were obtained by static calculations with the relaxed lattice parameters and atomic positions. Here, we note that some static calculations for unrelaxed geometries were also performed for purposes of reference.

### 3. Simulation results and discussions

#### 3.1. Geometry

Relaxed geometries were obtained for both structures. However, the result for the sp\(^2\)-based structure is unfortunately equivalent to the sp\(^3\)-based one while the displacement by relaxation from the sp\(^3\)-based structure is almost negligible (< 0.1 Å, and is visually equivalent to Figure 1(b)). The obtained lattice parameters for the sp\(^2\)-based structure are \(a = 9.702\) Å, \(b = 7.504\) Å, \(c = 7.179\) Å, \(\alpha = 90.209^\circ\), \(\beta = 107.127^\circ\) and \(\gamma = 90.185^\circ\), which give a volume of 499.431 Å\(^3\), and those for the sp\(^3\)-based structure are \(a = 9.662\) Å, \(b = 7.516\) Å, \(c = 7.118\) Å, \(\alpha = 89.998^\circ\), \(\beta = 107.476^\circ\) and \(\gamma = 90.005^\circ\), which give a volume of 493.061 Å\(^3\). The changes by relaxation and differences between the two structures are within the error margins expected from the precision of the calculation, i.e., a few percent. Consequently, the difference in the obtained geometries between the calculations for the two structures is found to be negligible since the differences in atomic positions are also within the calculation error margins.

Equivalent results were also found with harder PAW potentials and other functional types, i.e., GGA-PBE revised for solids [9] and the local density approximation (LDA), and with phenomenological van der Waals corrections (see Appendix A). This was also confirmed by distorting the initial geometry so that there was no local energy minimum to support the sp\(^2\)-based structure. Thus, it is concluded that the sp\(^2\)-based structure is unstable for the experimentally determined composition.

| Site  | \(X\)            | \(Y\)            | \(Z\)            |
|-------|------------------|------------------|------------------|
| La(1) | 0.3896 ± 0.0133  | 0.1418 ± 0.0039  | 0.5800 ± 0.0104  |
| La(2) | 0.0322 ± 0.0096  | 0.1261 ± 0.0008  | 0.7398 ± 0.0053  |
| Ge    | 0.3116 ± 0.0097  | 0.5919 ± 0.0060  | 0.5364 ± 0.0039  |
| O(1)  | 0.2974 ± 0.0086  | 0.0821 ± 0.0005  | 0.8500 ± 0.0046  |
| O(2)  | 0.3935 ± 0.0114  | 0.4583 ± 0.0143  | 0.7452 ± 0.0074  |
| O(3)  | 0.4041 ± 0.0067  | 0.7886 ± 0.0107  | 0.5138 ± 0.0141  |
| O(4)  | 0.1211 ± 0.0092  | 0.6336 ± 0.0010  | 0.4968 ± 0.0050  |
| O(5)  | 0.1233 ± 0.0105  | 0.1199 ± 0.0016  | 0.4501 ± 0.0066  |

Table 2 shows the atomic coordinates in the relaxed geometry. It should be noted that calculated values for the sp\(^2\)-based structure are employed hereafter. The equivalent positions fit within less
Table 3. Total energies of systems containing one oxygen vacancy per unit cell. The unit is eV.

| Vacancy site | sp\(^2\)-based | sp\(^3\)-based |
|-------------|-----------------|-----------------|
| O(1)        | -209.09         | -238.67         |
| O(2)        | -210.16         | -239.26         |
|             | -210.18         | -239.29         |
|             | -210.22         |                  |
| O(3)        | -212.07         | -239.88         |
| O(4)        | -214.13         | -238.87         |
| O(5)        | -211.75         | -236.62         |

Figure 2. Total electronic density of states for the relaxed geometry. The vertical line at energy 0 indicates the Fermi energy defined as the top of the occupied states.

than 0.015 standard deviations in fractional coordinates. It is understood that the difference from the experimental sp\(^3\)-based structure is also within a similar range to the standard deviations except for Z of O(3) which is 0.0385 because of its distorted initial configuration. The obtained Ge-O(1), Ge-O(2), Ge-O(3) and Ge-O(4) distances are 1.83, 1.79, 1.76 and 1.81 Å, respectively, and are classified as single bonds. Here, the La(2)-O(4), La(2)-O(5) and O(4)-O(5) distances become 2.49, 2.38 and 2.96 Å, respectively, by keeping them longer than the covalent bond lengths.

In order to investigate the effects of geometry on the tendency of oxygen vacancy formation, we performed total energy analyses on systems where one oxygen is removed from a unit cell based on static DFT calculations where all atoms are fixed. The analyses were made on the sp\(^2\)-based initial geometry and the (sp\(^3\)-based) relaxed geometry. It should be noted that the analyzed configurations are for simulating unstable domains to accept oxygen ions. The current analyses were made by assuming a neutral total charge where charge trapping around the vacancies is negligible. The results are shown in Table 3. The energies for equivalent positions of O(2) are spread while the remainder are identical within an error of 0.02 eV. The energy difference of about 30 eV between the two structures is in a similar range to the energy gain by geometric relaxation for the stoichiometric composition, which is 26.64 eV (from -221.84 to -248.48 eV). The lowest energy is found for O(4) in the sp\(^2\)-based structure while it is for O(3) in the sp\(^3\)-based one. The relative instability of O(5) vacancies suggests a large contribution of O(5) to the formation of LaO\(_2\) layers although the atomic distances and electronic properties do not indicate covalent features. Thus, if the sp\(^2\)-based structure is retained for some reason [6], the LaO\(_2\) layers will be favorable for oxygen vacancy formation while the LaGeO\(_3\) will be favorable in the sp\(^3\)-
based structure. It should be noted that the actual formation energies of oxygen ions should be lower than those evaluated from Table 3, considering the effects of geometric relaxation and charge compensation by electron trapping due to local metal-insulator transitions [10].

Figure 3. Partial electronic densities of states for the relaxed geometry projected onto valence (s, p, d and f) orbitals at each atomic site: (a), (b), (c), (d), (e), (f), (g) and (h) are for La(1), La(2), Ge, O(1), O(2), O(3), O(4) and O(5) sites, respectively.
3.2. Electronic density of states
The total electronic density of states obtained for the relaxed geometry was determined to be non-spin-polarized and is shown in Figure 2. The band gap of 4.029 eV indicates that this material is electronically insulating. It should be noted that the actual band gap can be larger since DFT-based calculations tend to underestimate it.

Contributions from each atomic orbital were extracted by obtaining the partial densities of states projected onto valence orbitals at each atomic site, which are summed over the magnetic quantum numbers (see Figure 3). It is understood that the portion from -5 to 0 eV mainly consists of p orbitals of oxygen and also contains small contributions from p orbitals of germanium and much smaller contributions from d orbitals of germanium and lanthanum. The similarity in the features between La(1) and La(2) indicates non-covalent interactions with the surrounding atoms where the details of the atomic coordinates are not significant. The p orbital portions for O(1), O(2), O(3) and O(4) are split into two parts by a gap from -3.0 to -2.5 eV while that for O(5) possesses only the upper part. Thus, the lower p portions for O(1), O(2), O(3) and O(4) form isotropic covalent bonding orbitals with the p orbitals of germanium. The upper p portions for the all oxygen sites overlap with the d orbital components of lanthanum and germanium. It is considered that this p-d interaction accounts for the La(2)-O(5) bonding.

4. Conclusions
It was clarified that stoichiometric La<sub>2</sub>GeO<sub>5</sub> contains sp<sup>3</sup>-type GeO<sub>4</sub> tetrahedral substructures in its stable atomic geometry and has a tendency to form oxygen vacancies in the LaGeO<sub>3</sub> layers. Although the formation mechanism of the distorted sp<sup>2</sup>-type GeO<sub>4</sub> substructures is still unclear, it is expected that the oxygen vacancies are more likely to be formed in the LaO<sub>2</sub> layers if the geometry is retained as reported in experiments. The contradiction regarding the geometry between the experiments may be due to the difference in the methods of sample preparation, which can cause unexpected element substitution, e.g., of lanthanum with strontium contained in the ingredients [6, 8].

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Appendix A. Parameters for van der Waals corrections

Phenomenological van der Waals (vdW) corrections based on the Grimme empirical force-field method [11] were made with parameters defined for each element: $C_6 = 185.1 \text{ J nm}^6 \text{ mol}^{-1}$ and $R_0 = 1.727 \text{ Å}$ for lanthanum, $C_6 = 17.1 \text{ J nm}^6 \text{ mol}^{-1}$ and $R_0 = 1.727 \text{ Å}$ for germanium, and $C_6 = 0.7 \text{ J nm}^6 \text{ mol}^{-1}$ and $R_0 = 1.342 \text{ Å}$ for oxygen, where $C_6$ and $R_0$ denote the dispersion coefficient and the vdW radius, respectively. The values for germanium and oxygen were based on the defaults of VASP version 5.2.11. $C_6$ for lanthanum was given by the definition $C_6 = 0.05 \times N I_p \alpha_D$ [11] with an ionization potential $I_p = 538.1 \text{ kJ mol}^{-1}$, a static dipole polarizability $\alpha_D = 210 \text{ a.u.}$ [12, 13] and a number of electrons of the rare gas element in the same row, i.e., radon, $N = 86$. There is no reliable data for the vdW radii of sixth-row elements in the public databases, however, so we took the value for lanthanum to be the same as germanium by assuming that the radii of the sixth-row transition metals and rare-earth elements are slightly smaller than platinum, whose value is considered to be $1.75 \text{ Å}$ [14].