Oxide Ion Conduction via Interstitial Sites in the Substituted Scheelite- and Spinel-type Oxides

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In the purely academic interests to find new and high oxide ion conductors, we investigated on the electrical conduction in the substituted scheelite- and spinel-type oxides. In the former, the substitution methods shown by Pb$_{2-x}$Ln$_x$WO$_{4+x/2}$ and Pb$_{2-x}$Ln$_{2-x}$WO$_4$ (Ln : Lanthanoid element) to intend to increase the concentration of defects brought about formation of the PbWO$_4$-based scheelite-type solid solutions, where the enhanced oxide ion conductivities were observed compared with that of the based material. From the structural and density measurements, the charge carriers in those phases were considered to be interstitial oxide ions. On the other hand, electrical conduction was also studied in many substituted spinel type oxides. Although the oxide ions would be generally hard to move considering from their cubic-packed form, the enhanced oxide ion conductivities were observed in the inverse spinel type solid solutions based on Zn$_2$TiO$_4$. A typical sample was Zn$_{2-x/2}$Ti$_{1-x}$Ta$_x$O$_6$, the ionic conduction of which was considered to be due to the interstitiality oxide ion migration. These results are mentioned in relation to the defect crystal phases.

Key Words: Oxide Ion Conductor, Scheelite-type, Lead Tungstate, Spinel-type, Zinc Titanium Oxide

1 Introduction

The stabilized zirconias are well-known as typical high-temperature-type oxide ion conductors with a fluorite-type structure. The perovskite- and pyrochlore-type oxides are also familiar to form typical groups of oxide ion conductors. Beside these materials, the oxide ion conduction have been investigated in some compounds with special crystal structures; although A. R. Cooper et al. and E. Sonder reported “Oxygen Diffusion” on MgAl$_2$O$_4$ in 1981 and 1983, respectively, the conductivities (or diffusion coefficients) were too low to regard the magnesium aluminate spinel as an oxide ion conductor. Following the spinel, there appeared a paper concerning to the vacancy motion in corundum, but the detailed conductivity or diffusion coefficient was not mentioned.

Thereafter, the apatite-type oxides were proved to be a group of high oxide ion conductors and declared the conduction mechanism.

On the other hand, beginning the study of the fast oxide ion conductors based on Bi$_2$O$_3$, the present authors have been investigating on high conductivity ion conductors; various kinds of samples have been prepared by the solid state reaction and their conduction properties have been studied by way of electrochemical methods. As a result, we have found new oxide ion conductors with unique crystal structures; the scheelite-type solid solutions based on PbWO$_4$, and the spinel-type solid solution shown by Zn$_{2-x/2}$Ti$_{1-x}$Ta$_x$O$_6$. Although oxide ion vacancies usually contributed to the oxide ion conduction in many conventional oxide ion conductors, the interstitial oxide ions played very important roles for oxide ion movement in the former case and the cation vacancies in the latter case. Their characteristic conduction properties will be mentioned together with their defect structures in the followings.

2 Scheelite-type Oxides

2.1 Crystal structure

CaWO$_4$ is called as the mineral “Scheelite”, which was named after K. W. Scheele. This oxide is generally classified into an oxysalt having a crystal structure corresponding to the deformed fluorite. Another typical example of the scheelite-type oxides is PbWO$_4$. Taking account of the electronegativity of each metal atom in these two oxides (Ca:1.04, Pb:1.55, and W:1.40 against O:3.50), the difference between Pb and W is pretty larger than that between Ca and W. Therefore, although the former is naturally seen as an oxysalt with a structure having Ca$^{2+}$ ions among WO$_6^-$ octahedrons, the latter may be considered as a double oxide with a deformed fluorite type structure; lead and tungsten atoms occupy the sites equivalent to calcium in fluorite in keeping an ordering arrangement, but oxygen atoms a little regularly shifted positions from those of fluorine by week tendency to make WO$_6$ tetrahedrons. As a result, the unit cell parameter (c-axis) must be taken twice larger and the total unit cell deformed tetragonal as indicated in Fig. 1. Furthermore, the scientific term, Double Oxide, makes us consider it to present a based compound of oxide ion conductor, as is so the perovskite-type oxides. Recently the electrical properties have been known for Fergusosite (YNbO$_4$) and/or Zircon (ZrSiO$_4$)-type oxides; these are also relative compounds to the present Scheelite.
be obtained. Unfortunately, this type of oxide solid solution was recognized not to form in a wide range. This may be because there exists the weak tendency to form WO$_3^-$ ions (that is, to hate the oxygen deficiencies) even in PbWO$_4$ that can be seen as a double oxide. In order to keep WO$_3^-$ as it is and create new oxygen defects, there was another substitution method; if a trivalent cation was able to be substituted for Pb$^{2+}$, excess oxide ion could be present in interstitial sites of the crystal, which would be attributed to the oxide ion migration.

We were able to prepare the solid solution samples shown by Pb$_{1-x}$Ln$_x$WO$_{4+x/2}$ where Ln is a lanthanoid element and La, Pr, Nd, Sm or Tb was actually adopted.$^{8,20}$ Another substitution was also possible; for example, the number of oxide ions seemed to be kept constant in Pb$_{1-x}$Ln$_{2x/3}$WO$_{4+x/2}$ In this case, however, a little excess (interstitial) oxide ions were found to form finally; this is apparent from rewriting the formula to shift some tungsten to original Pb and/or Ln sites without creation of the cation vacancies. As a result, these two formulae were to have principally the same substituting meaning. However, as a few points still remained vague as to the latter case, the system shown as Pb$_{1-x}$Ln$_x$WO$_{4+x/2}$ was mainly mentioned in the next section.

The samples of this system can be prepared by ordinary solid state reaction method using PbO, Ln$_2$O$_3$ and H$_2$WO$_4$ as the starting materials at high temperature near 1000 °C. Mechanical alloying method is also possible to get the powdery oxide, in which the particular conditions of defects are sometimes recognized.$^{21,22}$ However, when the ceramic samples were obtained finally by firing or sintering process for electrochemical measurements, all of them were to have excess oxide ions as shown by Pb$_{1-x}$Ln$_x$WO$_{4+x/2}$.

2.3 Ionic conduction in Pb$_{1-x}$Ln$_x$WO$_{4+x/2}$

By substitution of various lanthanoid elements, higher conductivity than that of the pure PbWO$_4$ was observed and the transport number of oxide ion was found to be almost unity under the atmosphere; that is, irrespective of the changeable valence of lanthanoid ions in the case such as Pr and Tb to be substituted, the conduction were mainly due to oxide ions in these system as was so in the other lanthanoid ion-substituted PbWO$_4$’s.$^{8,20}$ Of course, if these conductors were under a reduced atmosphere, the partial electronic conduction would appear by reductive reaction of the oxides. However, the oxide samples including interstitial oxide ions seemed to be superior to those without them against the partial reduction under lower oxygen partial pressures. These are the theses of our future investigation for conduction and stability on these oxide ion conductors.

The composition to form the single phase was determined in each system by X-ray diffraction. It was found that the solubility range was dependent on the ion radius of dopant; the larger, the wider. This means that as Ln was substituted for Pb, Ln$^{3+}$, which has the nearest ionic radius to Pb$^{2+}$, could be widely dissolved into PbWO$_4$. In Pb$_{1-x}$La$_x$WO$_{4+x/2}$, the solubility range actually extended to $x = 0.4$ at least. The highest conductivity was obtained at $\sigma = 6.0 \times 10^{-2}$ Scm$^{-1}$ at 800 °C for $x = 0.2$. 

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**Fig. 1** Schematic view of the scheelite-type PbWO$_4$ structure (unit cell). Pb, W and O atoms are represented by middle, small and large spheres, the radii of which are the halves of the ionic ones proposed by Shannon for convenience. The 8e sites (0 0 2) of $I/a$ symmetry with the equivalent position are depicted by the thin cross marks.

2.2 Preparation of substituted scheelite-type oxides

From the above characteristics again, it was reasonable to consider CaWO$_4$ as a based material of the cation conductors as same as the other oxysalts, because although the oxygen contents could not be changed in WO$_3^-$ tetrahedrons themselves, two monovalent alkaline ions might be substituted for a calcium ion keeping WO$_3^-$ tetrahedrons as they are; actually lithium ion conduction was found in the substituted samples of Ca$_{1-x}$Li$_x$WO$_4$. Of course, replacing calcium totally in CaWO$_4$ with the other alkaline earths such as strontium and barium, and tungsten with molybdenum, the same type structure can be obtained, which could also be based materials of cation conductors. On the other hand, considering the based materials suitable to oxide ion conductors by electronegativity, valence and ionic radius of the excluded atoms, there was no choice besides PbWO$_4$ and PbMoO$_4$, so far. Here, in order to get oxide ion conductors, the substituted samples based on PbWO$_4$ have been synthesized to have various oxygen contents (oxide ion vacancies or interstitial oxide ions), and the conduction properties were investigated at higher temperatures.

The easiest way to change oxygen contents is to substitute pentavalent cation for W$^{6+}$; when Nb$^{5+}$ was employed, the oxides shown by PbW$_{1-3}$Nb$_4$O$_{9-4x/2}$ might
sample (Fig. 2)\textsuperscript{26} which did not correspond to the sample composition with the most interstitial oxide ions. This reason is not clear, but may be due to association of the excess oxide ions as mentioned in the conventional fluorite-type conductors.

On the other hand, the activation energy, $E_a$ for oxide ion conduction can be calculated from Arrhenius plots in Fig. 2. In the higher temperature range above 600°C, the $E_a$ is 57 kJ mol$^{-1}$ for Pb$_{10}$La$_6$WO$_{41}$, and it grows up to 87 kJ mol$^{-1}$ in the lower temperature range. The $E_a$'s are likely to grow only a little larger in the both temperature ranges for the samples of $x > 0.20$ showing relatively lower conductivities. Considering that the $E_a$'s range from 82 kJ mol$^{-1}$ to 116 kJ mol$^{-1}$ for ZrO$_2$-based conductors,\textsuperscript{23} the $E_a$'s of the present system are not particularly high even in the oxide ion conduction due to interstitial oxide ions. This may mean that the interstitial oxide ions could be regarded as oxide ions covering in the hypothetical vacant sites on a pure scheelite-type (i.e. a distorted CaF$_2$-type) oxide, PbWO$_4$.

In any case, it was surprising that more than 5% excess interstitial oxide ions could be present in the present La-$\text{substituted PbWO}_4$ with the scheelite-type structure. We supposed that the good oxide ion conduction could be caused by the interstitial oxide ions in the solid solution region. The existence of interstitial oxide ions in the crystal was confirmed by comparing of the measured sample densities with the theoretical ones. However, we could not determine the oxygen position only by the measurement.

### 2.4 Position of interstitial oxide ion

Considering existence of the heavy metal cations of Pb and W, and the relatively low occupancy of interstitial oxide ion positions, time-of-flight (TOF) neutron diffraction experiments were carried out at room temperature in order to confirm the position of interstitial oxide ion.\textsuperscript{24} The oxide ion could be also discussed using infrared, impedance spectroscopy and/or heat capacity besides neutron diffraction, but the results would be mentioned elsewhere.\textsuperscript{25,26} Figure 3 shows the measured neutron diffraction pattern of Pb$_{1.5}$La$_6$WO$_{4+0.25}$ ($x = 0.2$). If the interstitial oxide ions were distributing holding $I4_1/a$ symmetry, only the 8e (0 0 z) and 16f sites were to be possible interstitial sites. Considering that the excess fluoride ion position in YF$_3$-doped CaF$_2$ has been believed to be near the unit cell center,\textsuperscript{27} we also expected the position near $z = 0.25$ in the 8e site corresponded to the center of the bottom half of the unit cell as an interstitial position.

We were searching the appropriate position from the occupation factors obtained by applying the Rietveld method, when the location of interstitial oxide ions was
moving along \( z \) at the 8e site (0 0 z). The refined occupancy factors for the oxide ion are plotted in Fig. 4, where tungsten and lead (or lanthanum) ions are present on the coordinates of \( z = 0 \) and 0.5, respectively, and the isotropic temperature factor \( B_{\text{iso}} \) of interstitial oxide ion is fixed to be 1.0 Å\(^2\). The occupancy profile showed a maximum around \( z = 0.3 \) with a small hump at \( z = 0.2 \). This means that if the occupancy was proportional to the probability of the interstitials, the interstitial oxide ion was to be at a little shifted position from the center (\( z = 0.25 \)) between Pb and W to the Pb direction. After the final refinement, the structural parameters were obtained. The results are represented in detail in the other previous paper\(^2\); considering that the lattice might be locally distorted by introduction of the interstitial oxide ions, the equivalent temperature factors were fairly enhanced. Occupation factors were also collected for the \( x = 0.1 \) sample (Pb\(_{0.9}\)La\(_{0.1}\)WO\(_{4}\)). The total tendency (closed circles in Fig. 4) resembled the results of \( x = 0.2 \). Although the main peak position was shifted toward the lead site and small hump toward the tungsten site, the results essentially supported the estimation of oxide ions made for the \( x = 0.2 \) sample. Based on the results that the interstitial oxide ions tended to be localized around \( z = 0.3 \) to 0.36 of the 8e site, the oxide ion conduction path can be presumed, which could correspond to that via \( F_{\text{at}}(1/2 \ 1/2 \ 1/2) \) in case of YF\(_3\)-doped CaF\(_2\).

### 3 Spinel-type Oxides

#### 3.1 Crystal structure

Contrary to the scheelite-type structure mentioned above, the mineral “Spinel”, MgAl\(_2\)O\(_4\) is crystallized into an oxygen-closest packed structure, where Mg and Al ions occupies 1/8 of tetrahedral and 1/2 of the octahedral sites formed by oxygen (Fig. 5), respectively. Because of a cubic closest packed structure of oxygen, it is generally believed that all the O-O distances are the same. However, these are subtly different depending on whether there are cations or not in tetrahedral and/or octahedral sites. Furthermore, the tetrahedral and octahedral sites without cation cannot be called as vacant sites; Mg\(_{0.5}\)Al\(_{0.5}\)O\(_{4}\) keeps its crystal structure itself as they are.

#### 3.2 Preparation of substituted spinel-type oxides

Taking account of another concept in the spinel, we know the words, normal, inverse and random spinels. In any case, it was impossible to introduce defects in closest packed oxygens themselves. In the course of our synthetic research of cation conductors, however, we surprisingly found that the cation-defective solid solution formed at room temperature in the substituted inverse
spinel type oxide \(\text{Zn}_2\text{Ti}_4\text{O}_9\), which could be a based material of ionic conductors \(\text{Zn}_2\text{Ti}_4\text{O}_9\). Considering the comparatively wide solid solubility of \(\text{MgO}\) or \(\text{Al}_2\text{O}_3\) to \(\text{MgAl}_2\text{O}_4\) at higher temperature over \(2000^\circ\text{C}\), it may not be an absolutely strange matter. However, the solid solution range is much narrower in lower temperatures under \(1000^\circ\text{C}\). Therefore, it is not clear why the obvious substitution is possible only in the inverse spinel-type oxide. As the cationic radii of \(\text{Zn}^{2+}\) and \(\text{Ti}^{4+}\) are relatively larger than those of \(\text{Mg}^{2+}\) and \(\text{Al}^{3+}\), the lattice constant (i.e. the O-O distance) of \(\text{Zn}_2\text{Ti}_4\text{O}_9\) is a little longer than that of \(\text{MgAl}_2\text{O}_4\) which may make the condition to introduce defects loose in \(\text{Zn}_2\text{Ti}_4\text{O}_9\). One more surprising thing to say is that the cation-deficient inverse spinel \(\text{Zn}_2\text{Ti}_4\text{O}_9\) was to be a based material of oxide ion conductors but not cation conductors. A typical substituted oxide was \(\text{Zn}_{2-x/2}\text{Ti}_{1-x}\text{Ta}_x\text{O}_4\) with some cation deficiencies, which was prepared by solid state reaction method using \(\text{ZnO}\), \(\text{TiO}_2\) and \(\text{Ta}_2\text{O}_5\) as the starting materials at high temperature near to \(1200^\circ\text{C}\).\(^{10}\)

### 3.3 Conduction properties in \(\text{Zn}_{2-x/2}\text{Ti}_{1-x}\text{Ta}_x\text{O}_4\)

Figure 6 shows the Arrhenius plots of conductivity in the system \(\text{Zn}_{2-x/2}\text{Ti}_{1-x}\text{Ta}_x\text{O}_4\) (\(x \leq 0.3\)), where the conductivity increases with increasing tantalum content (i.e. cation vacancy) and that the sample with \(x = 0.30\) has a conductivity of \(1.8 \times 10^{-3}\) S cm\(^{-1}\) at \(1000^\circ\text{C}\). The main charge carrier is oxide ion, which was confirmed by the fact that, in an oxygen gas concentration cell using air and pure oxygen as the anode and cathode gas, respectively, the measured EMF’s almost corresponded to the values by the Nernstian equation, and stable and steady currents could be drawn. More tantalum substitution resulted in the introduction of electronic conduction and the distortion of crystal structure from cubic to tetragonal system. Finally, a mixed phase was observed in the sample of \(x > 0.6\) and the conductivity obviously decreased.

In spite of the appearance of some electronic conduction, the activation energies, \(E_a\), for conduction are calculated from Arrhenius plots in Fig. 6, where the values gradually decrease from 174 kJ mol\(^{-1}\) to 105 kJ mol\(^{-1}\) with increasing Ta content. The value of 129 kJ mol\(^{-1}\) of the \(x = 0.30\) sample, which can be considered as an oxide ion conductor, is comparatively high compared with those of YSZ,\(^{25}\) which denotes a new oxygen diffusion mechanism except that via oxide ion vacancies. Pycnometric powder density measurement and Neutron diffraction results suggested that the oxide ion conduction in these spinel type phases was ascribed to interstitial oxide ion diffusion via cation vacancies. As these samples can be seen as typical oxides containing closest packed oxide ions in the crystals, the above oxide ion conduction was very interesting but unusual.

### 3.4 Role of cation vacancy in \(\text{Zn}_{2-x/2}\text{Ti}_{1-x}\text{Ta}_x\text{O}_4\)

The existence of cation vacancies in the crystal was  

![Arrhenius plots of conductivity measured in air for \(\text{Zn}_{2-x/2}\text{Ti}_{1-x}\text{Ta}_x\text{O}_4\).](image)

\(\text{O}: x = 0, \triangle: x = 0.05, \square: x = 0.20\) and \(\diamondsuit: x = 0.30\).

![Rietveld refinement neutron diffraction patterns of cubic phases of \(\text{Zn}_{2-x/2}\text{Ti}_{1-x}\text{Ta}_x\text{O}_4\).](image)

\(\text{Ta}_x\text{O}_4\) (\(x = 0.15\)).
supposed by comparing of the measured sample densities with the theoretical ones. In order to confirm the cation vacancies, Rietveld structure refinements were carried out on the Ta-substituted system, Zn_{2-ε}Ti_{1-ε}Ta_{ε}O_{4} with cubic symmetry. In advance of this analysis, the structure of cubic ZnTiO_{3} had been examined; as expressed conventionally by Zn[ZnTi]O_{6}, the tetrahedral cation sites (8a) was recognized to be occupied only by zinc ions and the octahedral ones (16d) by both zinc and titanium ions. The measured and refined diffraction patterns of the sample Zn_{1.925}Ti_{0.85}Ta_{0.15}O_{4} (x = 0.15 in Zn_{1.925}Ti_{0.85}Ta_{0.15}O_{4}) were shown in Fig. 7. Assuming tantalum ions in the octahedral sites regardless of the cation vacancy sites, the occupation factors were positive during the Rietveld operation. Furthermore, reliable factors $R_{wp}$ were compared among the next three typical vacancy models considering the different cation vacancy sites: Zn_{n-0.925}Zn_{0.925}Ti_{0.85}Ta_{0.15}O_{4} Zn_{n-0.9625}Zn_{0.9625} Ti_{0.85}Ta_{0.15}O_{4} and Zn_{n-0.9625}Zn_{0.9625} Ti_{0.85}Ta_{0.15}O_{4} where $\square$ denotes a vacancy. The obtained $R_{wp}$ values of 5.72, 4.95 and 4.52 for each configuration, respectively indicated that the cation deficiencies are preferentially formed at the octahedral sites. For the other compositions of cubic Zn_{1.925}Ti_{1-ε}Ta_{ε}O_{4} (x = 0.10, 0.12, 0.14 and 0.16), the procedure above resulted in essentially the similar defect structures.

Considering the oxide ion migration in the closely packed lattice, the interstitiality mechanism should be remembered. In order to ensure the oxide ion displace-

![Image](image.png)

**Fig. 8** (a) Variations of occupation factors of the interstitial oxide ion located on the line from an oxide ion to the tetragonal site ($\triangle$) and to the octahedral one (C) for cubic Zn_{2-ε}Ti_{1-ε}Ta_{ε}O_{4} (x = 0.15). Taking account of the number of equivalent site, the plotted $g(O)$ to the tetrahedral site was tripled for the comparison. (b) Schematic illustration of oxygen tetrahedron and octahedron to indicate the introduced interstitial position.

![Image](image.png)

**Fig. 9** Possible oxide ion migration mechanism as to vacant octahedral site.
not be observed, which indicated that an important factor for oxide ion conduction in the inverse spinel structure was not the substitution of different valence cation but the formation of cation vacancy. This fact also suggested the truthfulness of oxide ion movement shown in Fig. 9.

4 Summary

As new oxide ion conductors with unique crystal structures, the scheelite-type solid solutions based on PbWO$_4$ and the spinel-type solid solution based on Zn$_2$TiO$_4$ were found. In the former, the typical substitution method was shown by Pb$_{1-x}$Ln$_x$WO$_4$ (Ln : lanthanoid element), in which the enhanced oxide ion conduction was observed. In the latter case, the enhanced oxide ion conductivity was also observed in the inverse spinel type solid solution; a typical sample was Zn$_{2+x/2}$Ti$_{1-x/2}$Ta$_2$O$_6$. The defect crystal structures were investigated by the neutron diffraction analysis; as shown in the chemical formulae, interstitial oxide ion and cation vacancy were formed in Pb$_{1-x}$Ln$_x$WO$_4$ and Zn$_{2+x/2}$Ti$_{1-x/2}$Ta$_2$O$_6$ respectively. The crystallographic defect played very important roles in the oxide ion movement in each substituted oxide. In the latter case, especially, the oxide ion conduction was considered to be due to the typical interstitialcy oxide ion migration via cation vacancy. Based on these academic new findings, we are going to investigate novel and valuable oxide ion conductors.

References