

Metal-doped Pyrochlore as Novel Electrode Materials For Intermediate Temperature Solid Oxide Fuel Cell

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In this study, the metal-doped $\text{La}_2(\text{Zr}_{1-x}\text{W}_x)_2\text{O}_7$ (LWZO) pyrochlore phases were synthesized by Pechini sol-gel method and characterized by X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The phase width of tungsten is $x = 0.1 - 0.15$. Temperature-programmed reduction (TPR) shows that the as-prepared products are stable under hydrogen atmosphere. XPS measurements revealed the valence state of La^{3+} , Zr^{4+} , and $\text{W}^{(5+, 6+)}$. The ionic- and electronic- conductivity of the 15% W-doped LWZO is 2.2×10^{-3} to 1.9×10^{-2} S/cm from 400 to 700 °C, which is better than YSZ and GDC over this temperature range. The LWZO is stable up to 1400 °C under reduced atmosphere. Bottom cells were fabricated with the LWZO electrolyte and GDC. The results shown that the $\text{La}_2(\text{Zr}_{1-x}\text{W}_x)_2\text{O}_{7+\delta}$ have a good potential of becoming the electrolyte for IT-SOFCs.

Introduction

Solid oxide fuel cells (SOFCs) have been an intense research topic over the past two decades for their ability to convert fuel electrochemically to electricity. However, their high operating temperature (> 900 °C) can cause high degradation rate of cells and high cost for materials. The conventional electrolyte material used in HT environment is 8YSZ (8 mol% yttria-stabilized zirconia) oxide-ion conductor with fluorite type structure. Several alternative materials have been evaluated as electrolyte materials for IT-SOFCs. For example, doped CeO_2 (DCO) has been studied as an electrolyte material that exhibits high ionic conductivity compared to YSZ at 500-700 °C. The drawback for ceria-based material is its high electrical conductivity due to the reduction of $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ under low oxygen partial pressure at temperature above about 650 °C, which lowers open circuit voltage (OCV) and power performance. Perovskite ABO_3 -type materials have also been studied as fast oxygen ion conducting electrolyte, in doubly substituted gallates, giving a composition of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_y\text{Mg}_{1-y}\text{O}_{3-\delta}$ (LSGM). The levels of conductivity reported were higher than the YSZ in the 600-750 °C temperature range, but the stability of perovskite electrolytes still needs to be improved.

There have been some studies into materials with the pyrochlore structure $\text{A}_2\text{B}_2\text{O}_7$ (1, 2), which can be considered as a superstructure of a defective fluorite $(\text{A,B})\text{O}_2$ with one anionic vacancy per formula unit. The main difference with the ideal fluorite is the additional ordering in the cation and anion sublattices present in the pyrochlore structure. The partial loss of this ordering is a key point for ensuring the high ionic conductivity of these materials. These unoccupied sites provide pathways for fast oxygen transport.

Oxygen ion-conducting materials with pyrochlore structures have been studied since the 1960s. (3-6) Decreasing A-site cation radius favors the pyrochlore to fluorite transition. Usually, the maximum conductivity, which can be further enhanced by acceptor-type doping within the solid solution formation limits, occurs for cation stoichiometry (e.g. $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Zr}_2\text{O}_7$). Up to now, the highest level of oxygen ionic conduction in pyrochlore-type compounds was achieved for $\text{Gd}_{2-x}\text{Ca}_x\text{Ti}_2\text{O}_{7-\delta}$ with $x=0.20$ compares partial oxygen ionic conductivity of this material with data on other pyrochlores. (7-10)

Incorporation of calcium into the lattice of $\text{Gd}_2\text{Ti}_2\text{O}_{7-\delta}$ (11-13) increases p-type electronic conduction and decreases the n-type contribution to the total conductivity. In air, the electron transference numbers of $(\text{Gd,Ca})_2\text{Ti}_2\text{O}_{7-\delta}$ are close to the upper limit acceptable for solid electrolytes. Taking into account that ionic transport in $\text{Gd}_{2-x}\text{Ca}_x\text{Ti}_2\text{O}_{7-\delta}$ is lower than that in stabilized zirconia, the most likely applications of these pyrochlore are in SOFCs with thick-film electrolytes, or as protective layers applied onto $\text{LaGaO}_{3-\delta}$ or $\text{CeO}_{2-\delta}$ -based solid electrolytes. The moderate thermal expansion coefficients, Thermal expansion coefficient values of $\text{Gd}_{2-x}\text{Ca}_x\text{Ti}_2\text{O}_{7-\delta}$ (14, 15) ceramics enable compatibility with these materials. Another case is Mo doped GTO which has been shown to have a very high mixed ionic and electronic conductivity under reducing conditions, making it suitable as an anode material. It was found that the electrical conductivity of $\text{Gd}_2(\text{Ti}_{1-x}\text{Mo}_x)_2\text{O}_7$ is about 70 S/cm and 25 S/cm for $x = 0.7$ and 0.5, respectively, at $p(\text{O}_2)$ around 10^{-20} atm. However, this pyrochlore solid solution is only stable at a certain $p(\text{O}_2)$ range at high temperature. (16) In 1996, Shimura et al. has reported for some pyrochlore system with significant proton conductivity especially for $\text{La}_2\text{Zr}_2\text{O}_{7-\delta}$ -based systems, where proton incorporation is promoted by doping with lower valent cations on the A- or B-sites. (17) Higher proton conductivities are found for zirconates doped on the A-site. Proton conductivity of $(\text{La}_{1.95}\text{Ca}_{0.05})\text{Zr}_2\text{O}_{7-\delta}$ is 6.8×10^{-4} S/cm at 600 °C is three times larger than that of the system doped on the B site, suggesting differences in the proton concentrations. However, the total ion-conducting and other physical properties of these materials above are still below than YSZ and CGO, and so, their applicability remain limited.

The un-doped pyrochlore oxides usually exhibit low ionic conductivity. Challenges to prepare a pyrochlore phase with desired composition and properties include high sintering temperature and choices of substituted ions. In this study, we focus on the potential materials for applications in intermediate-temperature range (400 – 700 °C). The doping metal cations should be stable under a reducing atmosphere into the structure of pyrochlore structure for electrolyte. In order to increase the crystal defects, we doped foreign metallic cations to induce the formation of oxygen vacancies. $\text{La}_2\text{Zr}_2\text{O}_7$ host is what we choose because of its structural stability and the highest electronic conductivity value in the pyrochlore system.

Materials and Methods

Synthesis

$\text{La}_2(\text{Zr}_{1-x}\text{W}_x)_2\text{O}_7$ powders were synthesized by Pechni method, using stoichiometric ratio of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and controlled the dopant of Na_2WO_4 . The metal precursors were dissolved into DI-water serving as metal sources. Next, we mixed

with citric acid (CA) and ethylene glycol (EG) with molar ratio of metal ion solutions : CA : EG of 1 : 3 : 4. The mixture was stirred at 70 °C until the clear solutions turned into gel. The gel precursor was calcined at 350°C to remove the organic species then heated until 700 °C for 5 h to obtain the target products with white color. After grinding the powders, we washed it by di-water to remove the unreacted reagent, and check the product by powder X-ray diffraction spectrum.

Characterization

X-ray powder diffraction (PXRD) data of the products were measured at room temperature on a Bruker D8 Advance Bragg–Brentano-type powder diffractometer operated at 40 kV and 40 mA (Cu K α , $\lambda = 0.15418$ nm). For phase identification, XRD data were collected in a 2θ range from 20° to 70° with a step interval of 0.02°. The CELREF program was used for cell refinements. The morphology of products was examined with a scanning electron microscopy (JEOL JSM-6390LV SEM) with an accelerating voltage 10 kV. Temperature-programmed reduction (TPR) studies were performed in homemade units using powdered samples of 40 mg. The TPR experiments were carried out under a controlled gas mixture flowing through the sample at 200 mL·min⁻¹, raising the temperature at 10 °C min⁻¹ up to 900 °C. The consumption of hydrogen was monitored on-line with a thermal conductivity detector.

The surface composition and metal oxidation states of each samples were identified for fresh powder by X-ray photoelectron spectroscopy (XPS) on a KRATOS AXIS Ultra DLD spectrometer equipped with a hemispherical electron analyzer and an Al anode (Al Ka = 1486.6 eV) powered at 150 W with a pass energy of 20 eV. The peaks were referenced to the C 1s line at 284.5 eV. Background subtraction using the Shirley method and peak fitting to theoretical Gaussian–Lorentzian functions were performed using an XPS peak program.

The electron diffraction pattern and the tungsten dispersion uniformity were analyzed by JEOL JEM-2100 HRTEM, Gatan CCD 832 digital detector.

Conductivity Measurements

The conductivities of La₂(Zr_{1-x}W_x)₂O₇ (x = 0, 0.10, 0.15) were measured by a Solartron frequency response analyzer by supplying a voltage and the amplitude 100 mV to the sample at frequencies ranging from 0.1 Hz to 10 MHz using a Solartron frequency response analyzer. The mixed powders were pressed into pellets uniaxially at 4 tons/square inch of pressure and the pellets were calcined at 1400 °C for 5 h. SEM was used to check for the presence of porosity and grain structure. The density of the pellets was evaluated from the measurements of weight and dimension. The samples were heated in a homebuilt muffle furnace in flowing oxygen by 200 mL·min⁻¹, and the thermocouple was placed very close to the sample so as to minimize the temperature measurement errors.

Electrical conductivities were measured by Van der Pauw four-probe method. The four electrodes were W-Stainless wire. We measured the resistance of the test materials with a four-terminal ohmmeter by placing each pair of terminals on opposite ends of the test material. Then, we recorded the resistance of the test material.

Results and Discussion

Material Characterization

Figure 1(a) shows the PXRD patterns for $\text{La}_2(\text{Zr}_{1-x}\text{W}_x)_2\text{O}_7$. It is clear that the unreacted Na_2WO_4 could be removed in the reactions with $x > 0.15$, indicative of maximum doping amount. As can be seen in Figure 1(b), the refined lattice parameter changed from 10.73 to 10.83 Å. The trend is in reverse order because of the W^{5+} ion (0.62 Å) ion is smaller than Zr^{4+} (0.72 Å) ion. Although the ionic radius of $\text{W}^{5+,6+}$ (~0.62 Å) are less than that of Zr^{4+} (0.72 Å), the trend is in reverse order. It may be due to the effect of substituted $\text{W}^{5+,6+}$ with Zr^{4+} ions that create distorted coordination environments and lead to the expansion of unit cell.

Pressed ingots were heated and exposed under H_2 for 5 h at 700 °C. The color of the white pellet changed into greyish color. Figure 2(a) shows PXRD measurements after the experiment and there is no sign of decomposition. The crystallinity of ternary $\text{La}_2\text{Zr}_2\text{O}_7$ decreased and produced broad background peak at 2θ of ~30 °. On the other hand, the XRD pattern does not show any obvious change for W-doped samples $x = 0.05 - 0.30$. For comparison, the GDC powder was exposed under H_2 atmosphere for the same period of time and temperature, the PXRD patterns revealed remarkable changes in 30 ° and 40 ° for the formation of Gd_2O_3 .

The temperature-programmed reduction results show that there were no special signals around 100-900 °C, indicative of low activity under reduced condition, which is good for electrolyte material in SOFCs.

Figure 3(a) shows the La3d spectra contain two mainly splitting peaks around 840-865 eV for typical result for La^{3+} . The Zr3d orbital revealed two peaks around 180-185 eV for Zr^{4+} (Figure 6(b)). As the amount of doped-tungsten increased, the binding energy of the Zr3d orbital spectrum slightly shifted toward a lower energy because of a relative decrease of the Zr-O bonding energy. In Figure 3(c), we can see two peaks around 32.5-40 eV that are assigned as W^{6+} or W^{5+} . The results indicate that the valence state of tungsten atom may contain +6 and +5 states in the lattice. In terms of the results presented here, we propose the structure may contain vacancies in the B-site of Zr/W to form $\text{La}_2(\text{Zr}_{1-x}\text{W}_x)_{2-\gamma}\text{O}_7$ or extra oxygen in interstitial sites $\text{La}_2(\text{Zr}_{1-x}\text{W}_x)_2\text{O}_{7+\delta}$. The semi-quantitative analysis from XPS revealed the composition of Zr and W are 10.1 and 13.8%, respectively, which is close to the experiment (Table I)

Elemental analysis was carried out by EDX and inductively coupled plasma-atomic emission spectrometry (ICP-AES). The results indicate the upper limit of doped tungsten is about 0.13 in Table II. TEM element mapping clearly shows that the signal from tungsten element is observed in the powder. The particle size is about 15~20 nm, which is close to the result from PXRD calculations. The selected area electron diffraction (SAED) patterns of $\text{La}_2(\text{Zr}_{0.85}\text{W}_{0.15})_2\text{O}_7$ reveal diffractions corresponding to only pyrochlore phase (figure 4).

Electronic and ionic conductivity

Figure 5 shows the results of the electronic conductivity and ionic conductivity of

the powder pressing ingots. Ionic conductivity measurements were performed on the as-synthesized samples. The ionic conductivity of $\text{La}_2\text{Zr}_2\text{O}_7$ was 0.002 S/cm at 700 °C, but for W-doped LZWO exhibits a high conductivity, i.e., 0.018 and 0.019 S/cm at 700 °C for $x = 0.1$ and 0.15, respectively. The results indicated that doped tungsten was found to be an effective dopant for increasing the ionic conductivity.

The results indicate that the electronic conductivity of tungsten doped samples increased slightly compare to that of $\text{La}_2\text{Zr}_2\text{O}_7$. $\text{La}_2\text{Zr}_2\text{O}_7$ is the highest compared to other pyrochlore phases; nevertheless, the overall electronic conductivity is within 0.003 S/cm at 700 °C, which still lower than that of the conventional cathode and anode materials. Moreover, the ionic conductivity of W-doped samples increased significantly and comparable to that of the GDC as electrolyte material.

Conclusion

In this report, $\text{La}_2(\text{Zr}_{1-x}\text{W}_x)_2\text{O}_7$ solid solutions were synthesized by Pechini sol-gel method and analyzed by PXRD and XPS. We tried two pathways to obtain the final products. The first one was by the original sol-gel method and the other one was so-called the pre-washed sol-gel method. We successfully purified the product and achieved a mole ratio of $x = 0.3$. The XPS results showed that the valence of each metallic elements could be indicated by La^{3+} , Zr^{4+} , $\text{W}^{+5\sim+6}$, and O^{2-} , thus the formula of the structure was $\text{La}_2(\text{Zr}_{1-x}\text{W}_x)_2\text{O}_{7+\delta}$ by a general idea of charge balance. We also measured the electronic and ionic conductivity of these powders. In ionic conduction, the composition $\text{W } x=0.15$ was the highest one of these compounds. After comparing it with the undoped $\text{La}_2\text{Zr}_2\text{O}_7$ under H_2 reduction, the tungsten-doped pyrochlore structure was quite stable after redox. These compounds have potential for IT-SOFCs electrolyte material.

Acknowledgements

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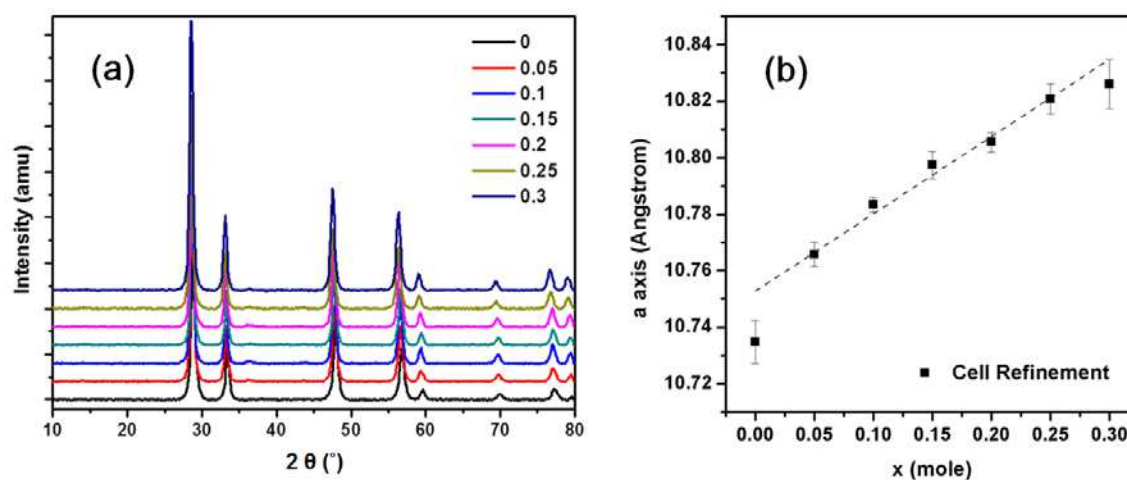


Figure 1. (a) PXRD patterns of $x = 0 - 25$ % $\text{La}_2(\text{Zr}_{1-x}\text{W}_x)_2\text{O}_7$ after 700°C calcined. (b) Comparison of the lattice parameter which was calculated by the program “Cell Refinement” to the doping percentage.

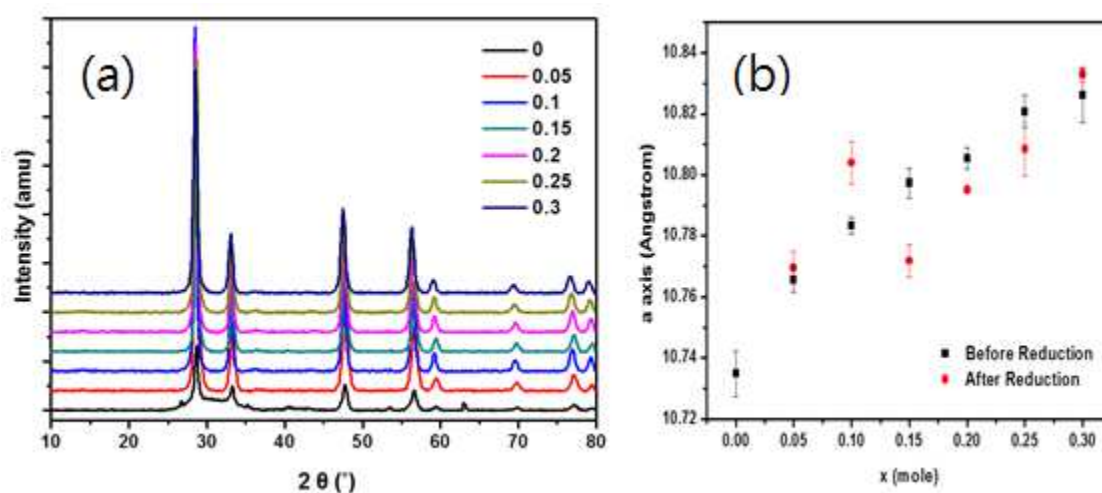


Figure 2. PXRD patterns of the ingots (a) reduction by H_2 for 5 hours at 700°C (b) The cell refinements of $\text{La}_2\text{Zr}_2\text{O}_7$ before reduction and after reduction.

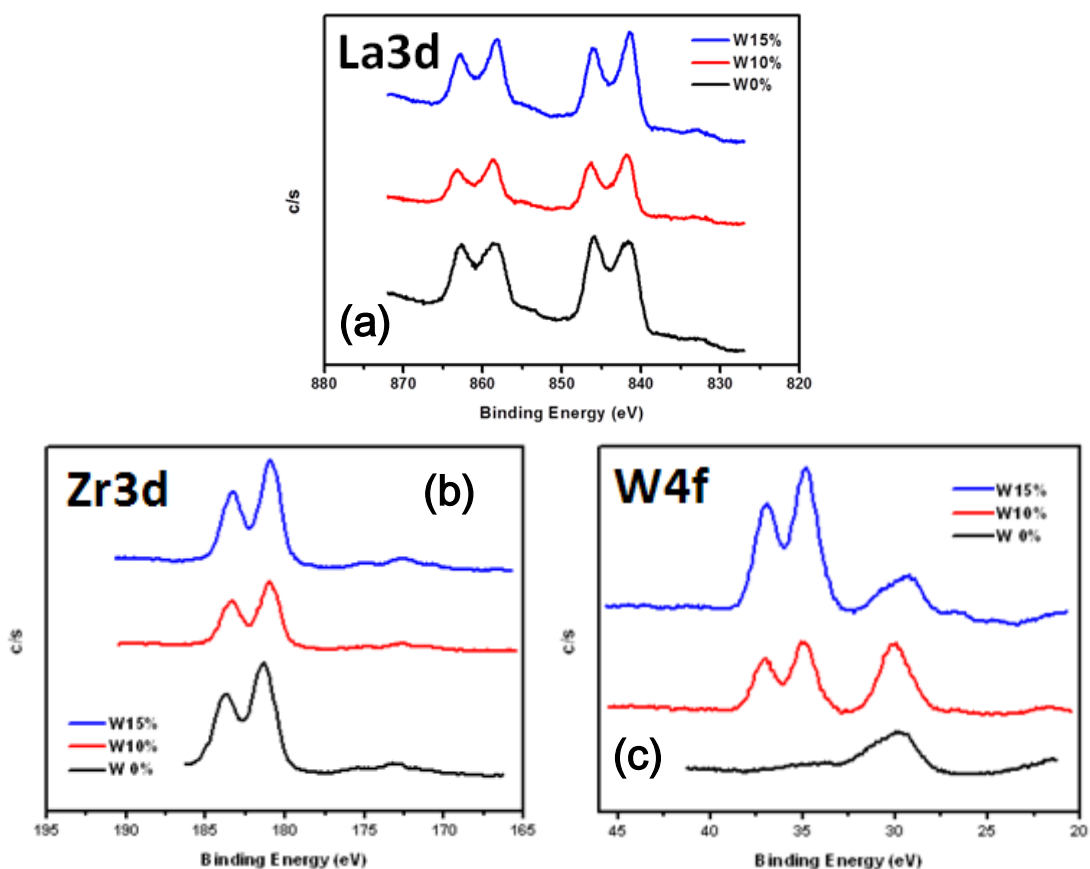


Figure 3. The XPS spectra of 0 - 15 % $\text{La}_2(\text{Zr}_{1-x}\text{W}_x)_2\text{O}_7$ (a) $\text{La}3d$ (b) $\text{Zr}3d$ (c) $\text{W}4f$.

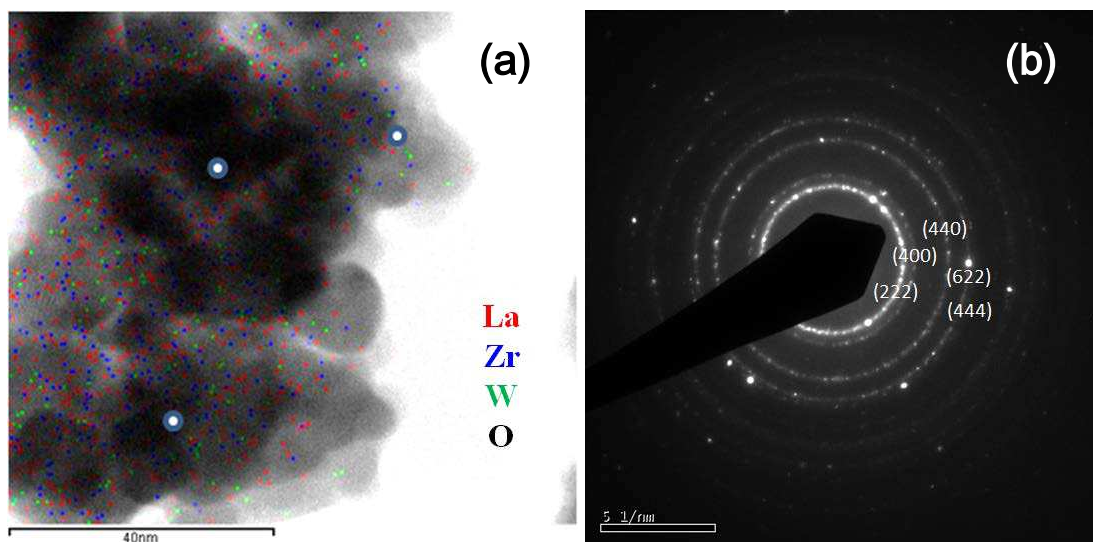


Figure 4 TEM analysis (a) EDS elemental mapping images (b) SAED patterns of $\text{La}_2(\text{Zr}_{0.85}\text{W}_{0.15})_2\text{O}_7$.

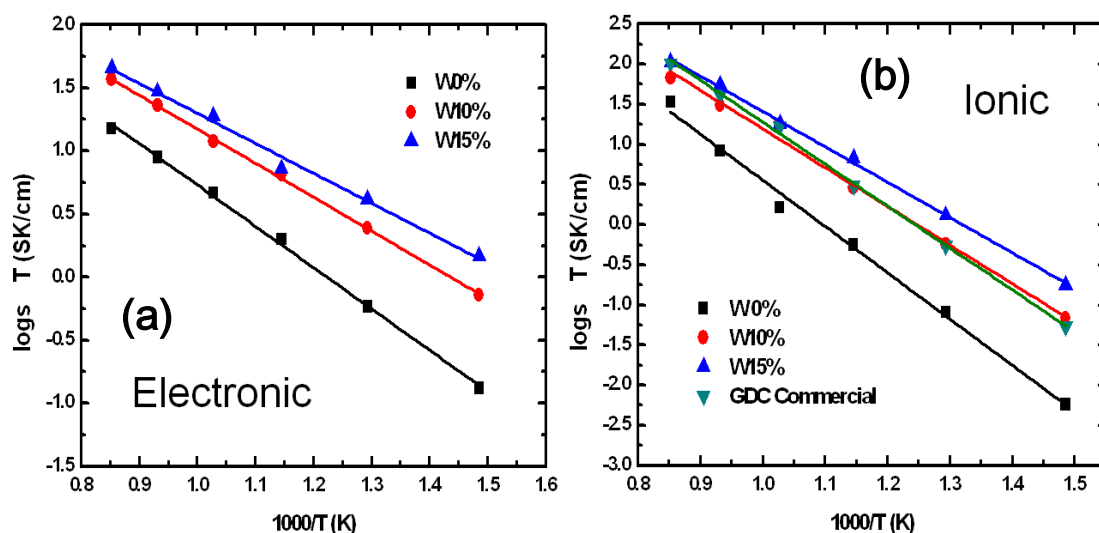


Figure 5 (a) Electronic conductivity of 0 - 15 % $\text{La}_2(\text{Zr}_{1-x}\text{W}_x)_2\text{O}_7$ (b) Ionic conductivity of 0 - 15 % $\text{La}_2(\text{Zr}_{1-x}\text{W}_x)_2\text{O}_7$ and comparison of GDC commercial powder.

Table I. The semi-quantitative datas of Zr and W through XPS spectra.

Sample	Zr3d(%)	W4f(%)
$\text{La}_2\text{Zr}_2\text{O}_7$	100	0
$\text{La}_2(\text{Zr}_{0.9}\text{W}_{0.1})_2\text{O}_7$	89.9(6)	10.1(4)
$\text{La}_2(\text{Zr}_{0.85}\text{W}_{0.15})_2\text{O}_7$	86.2(1)	13.8(5)

Table II. The semi-quantitative data of W(%) through ICP-AES and TEM-EDX spectra.

Mole ratio of W(%)	5	10	15	20
ICP-AES(%)	0.9	1.5	2.0	2.3
TEM-EDX(%)	3.1	5.3	7.3	8.6