Electrochemical properties of Cs-substituted CaWO_4 and BaWO_4 oxide ion conductors

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High-temperature electrochemical properties of Cs-substituted CaWO_4 and BaWO_4 have been investigated. When cesium ions are partly substituted for calcium site of Scheelite-type structured CaWO_4 to form oxide ion vacancies as $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$, oxide ion conduction appears at elevated temperatures. This defect structure for the oxide ion conduction is in contrast to the PbWO_4 -based oxide ion conductor with oxide ion interstitials, $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$. The measured electric conductivity of $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ ($x = 0.15$) is high as 10^{-2} Scm^{-1} at 750°C with the oxide ion transport number relatively close to unity. Essentially the similar results are obtained for the barium analogous system $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$, although the conductivity is still lower than CaWO_4 -based system.

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1. Introduction

Solid oxide fuel cell (SOFC) is one of the most attractive energy conversion systems for its high efficiency with low environmental impact.¹⁾ Since the solid electrolyte is a key component of SOFC, a lot of efforts have been done for the exploration of novel oxide ion^{2)–5)} or proton conductors.^{6)–10)} Scheelite-type structured PbWO_4 exhibits high oxide ion conduction at elevated temperatures by substituting trivalent lanthanum ions instead of divalent lead ions forming oxide ion interstitials as $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$.^{11),12)} We have intensively studied on this oxide ion conductor in terms of electrochemical and defect structural point of view.^{13)–22)} Pycnometry confirmed the formation of interstitial defect¹²⁾ and neutron diffraction study revealed the localized oxide ion interstitial sites as well as the estimated oxide ion conduction path.¹⁷⁾ On the other hand, CaWO_4 with the mineral name of Scheelite does not show such oxide ion conduction even by the lanthanum substitution with very narrow solid solution range. Nevertheless, twice amount of lithium substitution against the cation deficiency to form $\text{Ca}_{1-x}\text{Li}_x\text{WO}_4$ results in the lithium ion conduction.^{23),24)} Neutron radiography experiments indicated that only the lithium ion interstitials migrate in the lattice fixing the substituted lithium ion at the regular site.²⁴⁾

Most of fluorite-type structured oxide ion conductors utilize oxide ion vacancies for the ionic diffusion, e.g. stabilized zirconias,²⁵⁾ doped cerias²⁶⁾ or $\delta\text{-Bi}_2\text{O}_3$.²⁷⁾ Since Scheelite-type structure is closely related to the fluorite-type,²⁸⁾ aliovalent substitution to form oxide ion vacancy rather than interstitial is thought to be suitable for the oxide ion diffusion in CaWO_4 . Assuming that only the lithium ion at the interstitial site is mobile and that occupying at Ca site is not for $\text{Ca}_{1-x}\text{Li}_x\text{WO}_4$,²⁴⁾ substitution of equimolar amount of alkaline ions for calcium sites does not form

the mobile alkaline ion interstitials but the oxide ion vacancy for oxide ion diffusion. In addition, simulation study suggested that intrinsic defect of CaWO_4 is Frenkel-type and the formed oxide ion vacancy would be mobile.²⁹⁾ In the present study, monovalent alkaline ion is substituted for calcium in CaWO_4 to form oxide ion vacancy due to the electroneutrality, and cesium ion is selected as a substituent to prevent the alkaline ion conduction for its larger size. $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ has been synthesized to clarify the solid solubility, ionic conductivity, and conduction species. We have also examined the barium analogous system $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ to compare the properties with the former system.

2. Experimental

$\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ and $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ samples have been prepared by high-temperature sintering method starting from CaCO_3 , BaCO_3 , H_2WO_4 and Cs_2CO_3 . The calcining and sintering temperatures are selected as 800°C and 1000°C , respectively. Crystalline phases of the obtained samples were confirmed by powder X-ray diffraction (Shimadzu XRD-6000) with $\text{CuK}\alpha$ radiation (30 kV, 15 mA).

Platinum paste was applied on both sides of the surface of the synthesized samples with cylindrical shape (7 mm in diameter and 4 mm in length), and then baked at 800°C to form the porous Pt electrodes. Electric conductivity measurements were carried out in air by two-probe a.c. method using an impedance analyzer (HP 4192A) in the frequency range between 5 Hz–5 MHz. The major charge carrier was evaluated by the EMF measurements based on the oxygen gas concentration cells using the sample disks (10 mm in diameter and 1 mm in thickness) as electrolytes. The anode and cathode gases supplied were pure oxygen gas [$P(\text{O}_2) = 1 \text{ atm}$] and air [$P(\text{O}_2) = 0.21 \text{ atm}$], respectively. In addition to the oxygen gas concentration cell, proton conduction was also examined by constructing the steam pressure concentration cells, where the saturated vapor pressures were employed.

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3. Results and discussion

3.1 $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$

Figure 1 shows X-ray diffraction patterns of synthesized $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ ($x = 0$ to 0.2) samples. Since additional diffraction peaks presumably due to Cs_2CO_3 appear above $x = 0.175$ as depicted by triangle symbols, Scheelite-type structured solid solution ranges for $x \leq 0.15$. This solid solution range is narrower than that of $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ system with oxide ion interstitials ($x \leq 0.3$).¹¹⁾

Arrhenius plots of conductivity for $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ ($x \leq 0.2$) are represented in **Fig. 2**. For doped samples, conductivity is enhanced from that of the pure CaWO_4 by 1 or 2 orders of magnitude above 700°C . In comparison with $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ ($x = 0.2$) oxide ion conductor plotted by dashed line, conductivity data for the present $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ system are smaller by a half or one order of magnitude, and the conductivity of CaWO_4 -based system seems to rapidly descend with decreasing temperature below 700°C . Conductivity isotherms at 700 , 800 and 900°C are plotted in **Fig. 3**, where the conductivity increases almost linearly with Cs-substitution up to $x = 0.15$ of the solubility limit, thereafter it drops at $x = 0.175$. Concerning that the number of created oxide ion vacancy is proportional to the substituted cesium ions in the solid solution range for $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$, oxide ion

Fig. 1. X-ray diffraction patterns of $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$. Additional diffraction peaks due to the second phase is indicated by triangles.

Fig. 2. Arrhenius plots of conductivity for $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$. ●: $x = 0$, △: 0.05 , ○: 0.10 , □: 0.15 and ▽: 0.20 .

conduction mechanism is supposed to be vacancy diffusion. To determine the charge carrier, oxygen gas concentration cell has been constructed using sample disk as an electrolyte and EMF is measured. The measured EMFs of the cells are represented in **Fig. 4** for the samples $x = 0.10$ (○) and 0.15 (□). Since the obtained EMFs are relatively close to the calculated value assuming the Nernst equation (dashed line), the major charge carrier in this system is ions and electronic contribution is rather small. Moreover, stable current can be drawn from the cell as shown in the inset, indicating that predominant charge carrier is not cation such as cesium ion but oxide ion available at cathode. To confirm the immobility of cesium ions, d.c. field has been applied on the sample disk of $\text{Ca}_{0.85}\text{Cs}_{0.15}\text{WO}_{3.925}$ at 1000°C and then sample is cooled down to room temperature with keeping electric field. **Figure 5** shows SEM-EDX images for the cross section of a polarized sample, where (b), (c) and (d) denote the distribution map of W, Ca and Cs, respectively. Since any apparent segregation of cesium is not seen against other ions, cesium ion is not a major charge carrier in this system.

Considering that Cs substitution is designed to create oxide ion vacancy, and in addition, CaWO_4 unit cell possesses enough room to involve small amount of lithium ion interstitials as $\text{Ca}_{1-x}\text{Li}_{2x}\text{WO}_4$,^{23),24)} H_2O might be introduced at the oxide ion vacancy to enable proton conduction in the lattice. A water vapor

Fig. 3. Conductivity isotherms of $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$. △: 900°C , ○: 800°C and □: 700°C .

Fig. 4. (a) EMF versus temperature relation of the following oxygen gas concentration cell, Air ($P_{\text{O}_2} = 0.21$ atm) | $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ | O_2 ($P_{\text{O}_2} = 1.0$ atm). ○: $x = 0.1$, and □: $x = 0.15$. Dashed line: Nernstian value. Inset: discharge curve of the above cell using the sample ($x = 0.15$) as electrolyte.

Fig. 5. SEM-EDX images of the cross-section of polarized $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ ($x = 0.15$). (a) SEM image, and distribution maps of (b) W, (c) Ca and (d) Cs.

Fig. 6. Measured EMF of the following water vapor pressure cell. Wet Air (H_2O saturated at 0°C) | $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ | Wet Air (H_2O saturated at 21°C). $\circ$: $x = 0.1$, and $\square$: $x = 0.15$. Dashed line denotes the Nernstian value.

pressure concentration cell has been constructed using sample disk as an electrolyte and EMF measurements were also carried out to examine proton conduction possibility. The measured EMF plotted in **Fig. 6** is considerably smaller than the calculated one assuming saturated water pressure at 0 and 21°C . Accordingly, the major charge carrier in $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ system should not be proton but oxide ion.

3.2 $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$

In terms of the atomic number of Ba next to Cs, BaWO_4 is expected to be favorable for the Scheelite-type structured solid solution with Cs rather than CaWO_4 . Thus $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ solid solution has been synthesized to investigate electrochemical properties comparing with CaWO_4 -based system. **Figure 7** shows X-ray diffraction patterns of $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$, where additional diffraction peaks due to the second phase appear at $x = 0.125$. This solid solution range of $x \leq 0.1$ is narrower than that of $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ system despite of the larger ionic radius of Ba^{2+} (156 pm) in comparison with that of Ca^{2+} (126 pm).³⁰⁾ Since the ionic radius of Cs^+ (188 pm) is even larger than that of Ba^{2+} , the substituted cesium ion is thought to be associated with oxide ion vacancy to relieve the local stress due to the substi-

Fig. 7. X-ray diffraction patterns of $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$. $x = 0$ –0.125.

Fig. 8. Electric conductivity of $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$. $\bullet$: $x = 0$, $\circ$: 0.10, and $\diamond$: 0.125.

tution of larger cation in these systems. Electric conductivity of $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ is represented in **Fig. 8**. Although conductivity value enhances from the pure BaWO_4 , it does not attain to that of $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ ($x = 0.20$; dashed line) or even $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ ($x = 0.15$; dotted line) systems. The measured EMFs of oxygen gas concentration cells are relatively close to the calculated one as shown in **Fig. 9** and stable current is also drawn from the cell. Moreover, the vapor pressure concentration cell does not exhibit EMF. Therefore, the major charge carrier in $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ system is also oxide ion as $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$.

3.3 Comparison with $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ system

In the present study, it has been found that Scheelite-type structured oxysulfate (oxide sulfite), CaWO_4 and BaWO_4 , exhibit oxide ion conduction by forming oxide ion vacancy due to Cs ion substitution. Although oxide ion migrates presumably via the vacancy diffusion, conduction path would not be quite different from that of interstitial-type $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$, where mobile oxide ion moves through the regular and interstitial sites.¹⁷⁾ In **Fig. 10**, the activation energies of electric conductivity are evaluated at elevated temperatures (700 – 900°C), where the slopes of Arrhenius plot become gentle comparing with that below 700°C and oxide ion motion is almost activated. E_a s of $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ and $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ represent larger activation energies in comparison with $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$. One of the reason

Fig. 9. Measured EMF of the following oxygen gas concentration cell. Air ($P_{\text{O}_2} = 0.21 \text{ atm}$) | $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ ($x = 0.10$) | O_2 ($P_{\text{O}_2} = 1.0 \text{ atm}$).

Fig. 10. Compositional dependence of activation energies of conductivity. ●: $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$, ○: $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ and □: $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$.

for the enhancement in E_a is the difference in electronegativity between the two types of cations in the Scheelite-type structure,²¹⁾ i.e. Ca (1.00) or Ba (0.89) to W (2.36) in comparison with Pb (2.33 Pauling units) to W.³¹⁾ Larger electronegativity difference between the two cations would increase the potential energy barrier in the oxide ion conduction path. In addition, assuming that the regular oxide ion site is more stable than interstitial site, oxide ion vacancy in $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ or $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ is unlikely to move in comparison with oxide ion interstitial in $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$. While oxide ion interstitial in $\text{Pb}_{0.8}\text{La}_{0.2}\text{WO}_{4.1}$ delocalizes at relatively lower temperature as 200°C,²⁰⁾ higher temperature should be necessary to activate vacancy diffusion of oxide ion in the present system. The association of oxide ion vacancy to the substituted Cs ion should also attribute to enhance the activation energy. The increased activation energy for $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ below 700°C also support the association or some kind of ordering of oxide ion vacancy. While this is our first report on the CaWO_4 or BaWO_4 -based oxide ion conductors, further precise investigation should be made emphasizing on the defect chemistry to compare with interstitial-type PbWO_4 -based oxide ion conductors.

4. Conclusion

Oxide ion conduction has been found in Scheelite-type structured oxysalt CaWO_4 or BaWO_4 by partly substituting Cs ions to form oxide ion vacancy as $\text{Ca}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$ or $\text{Ba}_{1-x}\text{Cs}_x\text{WO}_{4-x/2}$. EDX analysis and EMF measurements of oxygen gas and vapor pressure concentration cells confirmed that the pre-

dominant charge carrier of the present systems is not cation or proton, but oxide ion. In contrast to $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ oxide ion conductor with oxide ion interstitial, the present system shows lower conductivity with higher activation energy. The enhanced activation energy is supposed to be caused by the difference in the electronegativity of oxysalt or vacancy diffusion mechanism.

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