Synthesis of Plate-Like (Ce,Sr)PO₄ and Preparation of Oriented Film by Electrophoretic Deposition Method

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In recent years, a hydrogen permeation film using a proton-electron mixed conductor has drawn much attention as a hydrogen-production process. In this work, we focus on (Ce,Sr)PO₄ with the monazite-type structure as the mixed conducting ceramics, and aim to synthesize the plate-like powder by means of the hydrothermal method. As a result, it is found that micaceous powders with the single phase can be obtained successfully. From crystal-structure analyses using synchrotron X-ray diffractions, it is suggested that Sr replaces Ce in the crystal and thus (Ce,Sr)PO₄ can be synthesized. This result is also supported by the electrical-conductivity measurements. In order to tailor an oriented film of the orthophosphate, we perform the electrophoretic deposition using the plate-like powders. As a result, it is demonstrated that the deposited film can be obtained by adding Li into an acetone deposition bath and the deposition amount can be controlled by the deposition voltage and time. It is also found that the prepared film tends to be oriented by applying lower deposition voltage.

**Keywords**: Electrophoretic Deposition, Hydrothermal Synthesis, Rare-Earth Orthophosphate, Oriented Film

1. Introduction

Hydrogen energy technologies without heavy environmental load have been expected to be realized in recent decades, and a great deal of effort has been devoted to establish a hydrogen-permeable film for hydrogen production 1-2. From such background, perovskite-type oxides with proton-electron mixed conduction and metals such as Pd have been investigated actively because these materials exhibit hydrogen-permeable property. Since the materials are not commercialized widely due to a cost issue and/or chemical stability, a development of a novel material with the mixed conduction is highly expected nowadays. As one of the promising candidates, we have focused on monazite-type rare-earth orthophosphates because the oxide-acid salts can be prepared easily and are stable chemically and thermally. Through the systematic works, it was found that Sr-substituted CePO₄, i.e. (Ce,Sr)PO₄, showed a proton-electron hole mixed conduction and thus a selective hydrogen-gas permeability 3-4. According to the previous works, it is considered that hydrogen gas is decomposed into proton and electron in the crystal and their conductions result in hydrogen-gas permeation. Therefore, an oriented film is regarded as preferable since the film can align the conduction pathway. However, such a film cannot be fabricated easily at the moment.

From such background, we synthesized plate-like (Ce,Sr)PO₄ powder by means of the hydrothermal method, and then tried to prepare the oriented film by the electrophoretic deposition (EPD) method using the plates. The deposited films were characterized by X-ray diffraction and scanning electron microscopy analyses, and effects of the deposition condition on the orientation characteristic were investigated.

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2. Experimental

2.1 Powder synthesis and characterization

Plate-like (Ce,Sr)PO₄ was prepared by the hydrothermal method using CeSO₄·4H₂O, SrSO₄, and H₃PO₄ as starting materials 4-5. CeSO₄·4H₂O and SrSO₄ with a molar ratio of 0.97:0.03 were dissolved into 50 mL of distilled water so that the total metal concentration became 0.1 mol·L⁻¹, and then 0.025 mol of H₃PO₄ was added. The [Ce]:[Sr] ratio was determined according to a previous work 6. The solution was transferred to a Teflon-coated stainless-steel vessel with a capacity of 100 mL, and then heat-treated at 180°C for 6-72 h. A precipitate was filtered, and then calcined in air at 1000°C for 30 h in order to obtain an orthophosphate from Sr-doped Ce₆(PO₄)₃HPO₄·H₂O 7-8. As a reference, CePO₄ without Sr substitution was also synthesized in the same manner.

The powders were identified by laboratory X-ray diffraction measurements (XRD: X’Pert Pro, PANalytical). In order to investigate the crystal structures and electron-density distributions in detail, synchrotron X-ray diffraction patterns were measured with a wave length of 0.05 nm at BL02B2 installed at SPring-8, Japan. The measurements were performed at room temperature with sample spinning. The recorded data were analyzed by the Rietveld technique (Rietan-FP99) and the maximum entropy method (MEM: Dynsormia 9). The results were visualized by the VESTA program 10. Morphologies of the powders were observed by the scanning electron microscopy (SEM: S-2600N, Hitachi High-Technologies). For the purpose of electrical-conductivity measurements, the samples were pelletized by a uniaxial pressing at 40 MPa, and then sintered in air at 1300°C for 10 h with an intermediate grinding. Pt porous electrodes were made on both sides of the pellets (ca. 10 mmφ and 1 mm thickness) by firing Pt paste. The measurements were carried out at 450-800°C by an AC two-probe impedance method (3532-50, HIOKI) with a fre-
frequency range from 42 Hz to 5 MHz. The atmospheric condition was controlled to a wet oxidizing condition where partial pressures of water vapor and oxygen were 4.2 and 100 kPa, respectively, by bubbling oxygen gas through water at 30 °C. In this paper, conductivities were calculated from total resistances which were estimated from intersects with the horizontal real axis of the Nyquist plot.

2.2 Electrophoretic deposition

In order to obtain an oriented (Ce,Sr)PO₄ film by the electrophoretic deposition (EPD), plate-like powder with a weight of 0.025–0.1 g was dispersed in acetone (100 mL) by an ultrasonic wave treatment at 28 kHz for 5 min (B1210J- MTH, Branson). As a dispersant, I₃ with a weight of 5–20 mg was added to the solution. According to literatures 17–32, this addition with tiny amount of H₂O in the bath results in proton formation and then powder in a bath gets charged positively:

\[
\text{CH}_3 + \text{H}_2\text{O} + \text{I}^- \rightarrow \text{CH}_3\text{OH}^- + \text{H}^+ + \text{I}^- \quad (2)
\]

A substrate for the EPD was a Ni foil with a fixed area of 5.5 cm² by masking using Nitoflon adhesive tape, and a counter electrode was a Ni foil with an area of 6.0 cm². A distance between these electrodes was fixed at 1.0 cm, and then a DC voltage was applied at room temperature for 0–3 min with the voltage range from 100 to 200 V (EX-375U2, Takasago). A deposited film was dried, and then a deposited amount was estimated by measuring weights of the film and a substrate to investigate effects of I⁻ and sample concentrations in the EPD bath. Finally, we sintered the film in air at 1300 °C for 5 h, and characterized the product by XRD and SEM in the same manner as the pristine powder. The film thickness was also estimated by SEM observation of the cut plane of the film.

### Table 1 Refined structure parameters of (a) CePO₄ (72 h) and (b) (Ce,Sr)PO₄ (72 h).

(a) Lattice parameters: \(a = 0.679718 \) 5 nm, \(b = 0.702333 \) 5 nm, \(c = 0.646952 \) 5 nm, \(\beta = 103.4590 \) 5°, \(V = 0.300365 \) 3 nm³.

<table>
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<th>Site</th>
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(b) Lattice parameters: \(a = 0.679843 \) 5 nm, \(b = 0.702560 \) 5 nm, \(c = 0.647329 \) 5 nm, \(\beta = 103.476(5) \)°, \(V = 0.300670 \) 3 nm³.

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3. Results and discussion

3.1 Synthesis and characterization

In order to prepare plate-like (Ce,Sr)PO₄ by the hydrothermal process, we investigated an effect of the treatment time keeping the temperature at 180 °C. Fig. 1 shows X-ray diffraction patterns of these samples after the calcination at 1000 °C for 30 h. In the measurements, the powders without grinding were loaded on a glass holder for the purpose of orientation investigation. These patterns indicate that the prepared samples have a single phase of the monoclinic structure (Space group: \(P2_1/n\)) as well as CePO₄. This result was supported by the Rietveld refinement as described below. It is also found that diffractions from (200) plane are outstanding compared with others, indicating that the samples have plate-like morphology. For the purpose of a detailed structure analysis, we measured synchrotron X-ray diffraction patterns and then performed the Rietveld and MEM analyses on both the (Ce,Sr)PO₄ and CePO₄ prepared hydrothermally. For the analyses, the powders were grinded sufficiently and then the

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**Fig. 1** X-ray diffraction patterns of hydrothermally-synthesized powders.
(a) (Ce,Sr)PO₄ (6 h); (b) (Ce,Sr)PO₄ (12 h); (c) (Ce,Sr)PO₄ (72 h); (d) CePO₄ (72 h)
diffraction patterns were recorded with sample spinning. As an example, the refinement pattern of the Sr-doped specimen is presented in Fig. 2(a), and refined structure parameters for both the samples are presented in Table 1. From this table, it is clarified that the lattice volume is slightly larger in (Ce,Sr)PO₄ than CePO₄. This suggests that a partial substitution of Sr for Ce was successful, considering a difference in the ionic radii. Such a substitution is also supported by a change in the sample color: that is, a color of (Ce,Sr)PO₄ was green due to mixed valence of Ce, whereas that of CePO₄ was white. The refined crystal structures and electron-density distributions are also depicted [Figs. 2(b) and (c)]. It is found that there is no significant difference in the structures of both the samples and all oxygens are bonded strongly with phosphorus forming PO₄³⁻ moieties. Such a result on the atomic and electronic structure of (Ce,Sr)PO₄ was essentially the same as in literatures on the material prepared by a different process, and thus this indicates that the preparation process does not have significant influence on the structures.

Fig. 2  Rietveld refinement pattern of (Ce,Sr)PO₄ (72 h) in the space group of P2₁/n. Plus marks show observed synchrotron X-ray diffraction intensities, and a solid line represents calculated intensities. Vertical marks below them indicate positions of allowed Bragg reflections. A curve at the bottom is a difference between the observed and calculated intensities in the same scale. This figure also presents refined crystal structures and electron-density distributions: (b) CePO₄ (72 h, wR₁ = 1.3 %) and (c) (Ce,Sr)PO₄ (72 h, wR₁ = 1.4 %). An isosurface level is 10¹⁵ e nm⁻³.

3.  Electrophoretic deposition

In order to prepare (Ce,Sr)PO₄ oriented films, we performed EPD using the plate-like (Ce,Sr)PO₄ which was synthesized with the hydrothermal method (180 °C, 72 h) followed by the calcination. Fig. 3 shows a deposited amount of (Ce,Sr)PO₄ as a function of an I₂ concentration. When we did not add I₂ in the deposition bath, the plate-like powder could not be deposited. By adding I₂, however, deposited films of the phosphate were successfully obtained on cathodes. This result should be due to a sufficient positive charge of the powder on the basis of the mechanism mentioned above (Eqs. 1 and 2). Since I₂ may cause unexpected reactions, I₂ amount should be optimized. From Fig. 3(a), it was found that the deposited amount was the largest.
when the I₂ concentration was 0.15 g·L⁻¹. Therefore, we fixed the concentration as this value hereafter. Fig. 5 also shows a deposited amount as a function of a sample concentration in the bath. As seen in this figure, the deposited amount becomes larger with increasing the sample concentration although the amount tends to be saturated around 1.0 g·L⁻¹. This means that the deposited amount can be controlled easily by the sample concentration in the deposition bath.

Fig. 4 Conductivities of the phosphates as a function of inverse of temperature. Circles and squares represent conductivities of (Ce,Sr)PO₄ (72 h) and CePO₄ (72 h), respectively.

Fig. 5 Deposition amounts as a function of (a) I₂ and (b) sample concentrations in the deposition bath. Deposition voltage and time were 100 V and 1 min, respectively. Sample concentration was 1.0 g·L⁻¹ for (a), and I₂ concentration was 0.15 g·L⁻¹ for (b).

Fig. 6 (a) Film thickness as a function of deposition time. Triangles, squares and circles represent deposition voltage of 100, 150 and 200 V, respectively. (b) Surface morphology of the film deposited under the condition that the voltage and time were 150 V and 2 min, respectively. Sample concentration was 1.0 g·L⁻¹ and I₂ amount was 0.15 g·L⁻¹.

On the basis of the above results, we investigated effects of deposition voltage and time on a film thickness while keeping sample and I₂ concentration as 1.0 and 0.15 g·L⁻¹, respectively. The results are presented in Fig. 6. It is clearly found that a film thickness increases with increasing both the deposition voltage and time, and can be controlled by changing these values. Fig. 6 (b) shows an SEM image of the film obtained by the EPD at 150 V for 2 min as an example. As seen in this image, the (Ce,Sr)PO₄ film can be successfully prepared by the EPD although the surface morphology is rough apparently. In addition, deposited plates seems to have smaller size than the synthesized plates (Fig. 3). This may be because plates with much larger size could not be deposited under the applied conditions. It was also found that lower deposition voltage than 150 V seems not appropriate because the morphology is not homogeneous.

X-ray diffraction patterns of some deposited films are presented in Fig. 7. The result demonstrates that the peak intensity from the (200) plane is stronger than the others. This indicates that the deposited films are orientated regardless of the EPD condition, reflecting the plate-like powder morphology. In order to evaluate degrees of orientation, intensity ratios of (200)/(120) diffractions, which is denoted as Rₒ, were calculated, and then the values were divided by a theoretical intensity ratio, Rₒ, for (Ce,Sr)PO₄ powder without orientation². From the Rₒ/Rₒ listed in Table 2, it is found that lower deposition voltage is preferable for preparation of the orientated film. Taking this fact into account, a higher deposition
Fig. 7 X-ray diffraction patterns of deposited films. Sample and \( I_1 \) concentrations were 1.0 and 0.15 g L\(^{-1} \), respectively. Deposition voltage and time were as follows: 
(a) 150 V, 2 min, (b) 150 V, 3 min, (c) 200 V, 2 min, (d) 200 V, 3 min

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speed may disturb an orientation process in the EPD. From these results, it can be concluded that an oriented \( \langle \text{Ce, Sr}\rangle \) PO\(_4\) film can be prepared by a simple and economical technique, i.e. the electrophoretic deposition, using hydrothermally-synthesized plate-like \( \langle \text{Ce, Sr}\rangle \) PO\(_4\), although the surface roughness should be improved in the future.

4. Conclusion
In this work, we synthesized \( \langle \text{Ce, Sr}\rangle \) PO\(_4\) with the hydrothermal method, and characterized the powder by the X-ray diffraction and scanning electron microscopy analyses. The results demonstrate that the powder is a single phase of the monazite structure and has a plate-like morphology. The detailed crystal-structure analysis and the conductivity measurement indicate that a partial substitution of Sr for Ce in CePO\(_4\) is successfully carried out. By using the plate-like \( \langle \text{Ce, Sr}\rangle \) PO\(_4\), we performed the electrophoretic deposition for the purpose of a oriented film preparation. It is found that the \( I_1 \) addition into an acetone deposition bath enables us to fabricate the deposited film and the deposition condition such as voltage and time determine the film thickness. It is also revealed that the oriented film can be obtained by the strategy although the surface roughness is insufficient.

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