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Effect of chemical state and occupation site of RE (RE = Yb, Y, Eu, Sm, Nd) on crystal structure and optical property of $BaCe_{1-x}RE_xO_{3-\delta}$ —Analyses of origin of peculiar crystal structure and property of $BaCe_{1-x}Nd_xO_{3-\delta}$

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ABSTRACT

Crystal structure, temperature dependence of molar volume and optical property of single phase $BaCe_{1-x}RE_xO_{3-\delta}$ were investigated. The crystal structure of $BaCe_{1-x}RE_xO_{3-\delta}$ (RE; Yb, Y, Eu, and Sm) and $BaCe_{1-x}Nd_xO_{3-\delta}$ changes from primitive orthorhombic to monoclinic and body-centered orthorhombic, respectively, by increasing x. Almost linear relationship between ionic radius of RE^{3+} and the molar volume are observed for $BaCe_{1-x}RE_xO_{3-\delta}$ with RE of Yb, Y, Eu, Sm; however, that of $BaCe_{1-x}Nd_xO_{3-\delta}$ is smaller than the relationship. As one of the origins, proposed is that Nd in $BaCe_{1-x}Nd_xO_{3-\delta}$ is near 4+, showing agreement with reported oxygen nonstoichiometry, in-situ X-ray absorption spectra and reduction expansion observed in this work. As another origin, partial Ba-site mixing of Nd^{3+} is proposed from separation of $BaCO_3$ from $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$ by high temperature sintering. The lower optical band gap of $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$ observed by reflectance spectroscopy, can also be explained by the partial mixing.

1. Introduction

$BaCe_{1-x}RE_xO_{3-\delta}$, where RE is rare earth ion such as Y, Yb, Sm, Nd and so on, attracts interest as high protonic conducting material with high transport number [1–23]. These oxides have been expected as a material for solid oxide fuel cells, H_2 gas sensor and so on. It has been reported that various properties and characteristics of $BaCe_{1-x}RE_xO_{3-\delta}$ are affected by kinds of RE. For example, Oishi et al. evaluated thermodynamic functions for water vaper incorporate reaction and electrical conductivity of various $BaCe_{1-x}RE_xO_{3-\delta}$ [22]. They concluded from the obtained thermodynamic functions and activation energy of electrical conductivity that $BaCe_{1-x}Nd_xO_{3-\delta}$ exhibited the electronic conduction besides protonic one whereas other $BaCe_{1-x}RE_xO_{3-\delta}$ show little electronic conduction. For the practical application of $BaCe_{1-x}RE_xO_{3-\delta}$, the optimization of RE must be carried out by the clarification of the origin of the difference of the properties by the kinds of RE. One possible origin is the difference of crystal structure by RE. Since protonic conducting property of $BaCe_{1-x}RE_xO_{3-\delta}$ appears at high temperature, the variation of crystal structure by temperature is also important information for the practical applications. However, reports on the difference of crystal structure of $BaCe_{1-x}RE_xO_{3-\delta}$ by RE, especially at high temperature are limited.

Another possible origin is different behavior of oxygen nonstoichiometry of $BaCe_{1-x}RE_xO_{3-\delta}$ by kinds of RE, which can be attributed to the difference of chemical state of RE at high temperature. Oishi et al. measured the oxygen nonstoichiometry of $BaCe_{0.9}RE_{0.1}O_{3-\delta}$ (RE = Y, Yb, Sm, Tb, Nd) by high-temperature equilibrium thermogravimetry [23]. They reported that oxygen content, 3-δ of $BaCe_{0.9}Y_{0.1}O_{3-\delta}$, $BaCe_{0.9}Yb_{0.1}O_{3-\delta}$, $BaCe_{0.9}Sm_{0.1}O_{3-\delta}$ and $BaCe_{0.9}Tb_{0.1}O_{3-\delta}$ were almost constant to be 2.95 between 600 °C and 1000 °C under 10^{-4} bar $\leq P(O_2) \leq 10^{0}$ bar, indicating that the valence of RE was fixed at +3 under examined conditions. They also reported temperature and $P(O_2)$ dependence of oxygen nonstoichiometry of $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$, which changed between 2.95 and 3.00 by the variation of temperature and $P(O_2)$. In $P(O_2)$ dependence of 3-δ of $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$ at 1000 °C, the plateau was observed at 2.95 under low $P(O_2)$ region, supporting valence of Nd was +3. At 500 °C under 1.0 bar of $P(O_2)$, the oxygen content was

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approximately 2.995, suggesting the valence of Nd approached +4 under such an oxidative conditions. Although tetravalent is uncommon chemical state for Nd ion, Oishi and co-workers reported that the valence change of Nd in $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$ by temperature or $P(O_2)$ could also be detected from X-ray adsorption near edge structure, XANES of Nd L_{III} and L_{II}-edge of $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$ at high temperature under controlled $P(O_2)$ [23]. Stevenson et al. reported that the difference of electrical conductivity and the weight variation of $BaCe_{1-x}Nd_xO_{3-\delta}$ between wet and dry conditions. They observed that the variation of electrical conductivity and weight variation of $BaCe_{1-x}Nd_xO_{3-\delta}$ by changing atmosphere from wet to dry was lower than those of $BaCe_{1-x}Yb_xO_{3-\delta}$ and $BaCe_{1-x}Gd_xO_{3-\delta}$ [24]. This showed correspondence with the results of oxygen nonstoichiometry reported by Oishi et al., indicating that the lower oxygen vacancy content of $BaCe_{1-x}Nd_xO_{3-\delta}$ than that of $BaCe_{1-x}Yb_xO_{3-\delta}$ and $BaCe_{1-x}Gd_xO_{3-\delta}$ under air.

As another possible origin, “A-site mixing” has been proposed. Tsur et al. prepared various kinds of $BaTi_{1-x}M_xO_{3-\delta}$ and investigated the molar volume. Linear increase was observed with increasing ionic radius if ionic radius of M ions was rather small. However, the deviation from the linear relationship was observed for $BaTi_{1-x}M_xO_{3-\delta}$ with rather large M ions [25]. They attributed the deviation to substitution of large M ion for not only Ti-site but also Ba-site, so-called “A-site mixing”. The “A-site mixing” model was also proposed for explanation of extraordinary small molar volume of $BaZr_{1-x}M_xO_3$ with large M ion [26] and $BaCe_{1-x}Nd_xO_{3-\delta}$ [27]. Wu et al. carried out measurements of extended X-ray absorption fine structure, EXAFS and insisted that “A-site mixing” was observed in $BaCe_{1-x}RE_xO_{3-\delta}$ [27]. However, their conclusion is not decisive due to insufficient sensitivity and resolution of EXAFS.

Since the change of the valence of RE, the variation of oxygen content and A-site mixing should involve lattice distortion, change of ionic radius and variation of site size, it can be expected that all of them can be detected by careful X-ray diffraction measurements at high temperature under various $P(O_2)$. The observation of impurity which generates from compositional deviation owing to A-site mixing can also be expected by X-ray diffraction with enough sensitivity. Also it is prospected that the variation of chemical state of RE and generation of defect originating from A-site mixing affect the optical property of $BaCe_{1-x}RE_xO_{3-\delta}$. In this study, the crystal structure, lattice constants and molar volume of $BaCe_{1-x}RE_xO_{3-\delta}$ at room temperature have been investigated and chemical state of RE has been deduced from the variation of the molar volume by kinds of RE. In order to distinguish whether the valence of RE varies or not by temperature or $P(O_2)$, high-temperature X-ray diffraction measurements have been carried out under various $P(O_2)$. To clarify that A-site mixing occurs or not, X-ray diffraction measurements with high intensity have been performed on $BaCe_{1-x}RE_xO_{3-\delta}$ prepared at various sintering temperatures under air or O_2. Optical property of $BaCe_{1-x}RE_xO_{3-\delta}$ at room temperature has been measured with diffuse reflectance spectroscopy to evaluate chemical state and occupation site of RE ions. It has been revealed that $BaCe_{1-x}Nd_xO_{3-\delta}$ shows peculiar crystal structure and optical property and their origins have been deduced.

2. Experimental

$BaCe_{1-x}RE_xO_{3-\delta}$ (RE = Yb, Y, Eu, Sm, and Nd) specimens were prepared by Pechini method from $BaCO_3$, CeO_2 and RE_2O_3. $BaCO_3$, which was dried at 150 °C for more than 12 h to remove the adsorbed moisture on the surface before weighing, was dissolved with aqueous solution of citric acid. CeO_2 and RE_2O_3 were dissolved with dilute HNO_3 containing citric acid and hydrogen peroxide solution, H_2O_2. After addition of ethylene glycol and citric acid to mixed solution with stoichiometric cation composition, the solution was fired at about 400 °C with mantle heater. The obtained resin was crushed to powdery state and pressed into pellets, and calcined at 850 °C for 12 h in air. The obtained pellets were crushed to powder and pressed into pellet again. The pellets were regularly sintered at 1300 °C for 10 h in air. As experiments to distinguish if A-site mixing occurred or not, the sintering at temperatures of 1300, 1350 or 1400 °C under air or O_2 was examined.

The crystal structures of $BaCe_{1-x}RE_xO_{3-\delta}$ at room temperature were evaluated by X-ray diffraction, XRD, measurements with high intensity (CuKα; 50 kV, 250 mA: RINT-2500, Rigaku Co., Ltd.). Temperature and $P(O_2)$ dependence of the crystal structure was analyzed with high-temperature XRD apparatus from room temperature to 1000 °C at interval of 100 °C under controlled $P(O_2)$ by flow ratio of O_2/N_2 mixed gases. The $P(O_2)$ was monitored by YSZ-based oxygen sensor set at downstream of the apparatus. Molar volume and its temperature dependence were estimated from the lattice constants, which were calculated from obtained XRD patterns.

For the evaluation of optical band gap, E_g, diffuse reflectance spectra were measured at room temperature between 200 nm and 1000 nm at interval of 1 nm using JASCO V-670 UV–VIS spectrometer employing integrating sphere. Scanning rate was 400 nm/min. As a light source, D_2 lamp and W lamp were employed for wavelength range shorter than and longer than 340 nm, respectively.

3. Results and discussion

3.1. Structural variation of $BaCe_{1-x}RE_xO_{3-\delta}$ (RE = Y, Yb, Eu, Sm, Nd) by kinds of RE and cation content

In our preceding paper [9], it was reported that the crystal structure of $BaCe_{1-x}Y_xO_{3-\delta}$ are orthorhombic distorted perovskite and monoclinic one for $0.00 \le x \le 0.10$ and $0.15 \le x \le 0.30$, respectively. In this study, the dependence of the crystal structure of $BaCe_{1-x}RE_xO_{3-\delta}$ on kinds of RE and RE content, x, has been investigated.

Fig. 1(a) shows XRD patterns of $BaCe_{1-x}Yb_xO_{3-\delta}$ at room temperature. All the peaks of $BaCe_{0.95}Yb_{0.05}O_{3-\delta}$ and $BaCe_{0.90}Yb_{0.10}O_{3-\delta}$ could be indexed as orthorhombic distorted perovskite with space group of *Pnma* (No. 62). With increasing x more than 0.10, the peak around $2\theta = 22.5°$, which was indexed as 111 of Miller index with *Pnma*, were not detected. The splitting of the peak around $2\theta = 20.0°$ observed for the specimens with x larger than 0.15 also indicated the structural phase transition from orthorhombic. All the XRD peaks of $BaCe_{1-x}Yb_xO_{3-\delta}$ with $0.15 \le x \le 0.30$ could be indexed as monoclinic distorted perovskite structure with space group of $P2_1/m$ (No. 11), showing similar tendency with the crystal structure of $BaCe_{1-x}Y_xO_{3-\delta}$.

Fig. 1(b) shows XRD patterns of $BaCe_{1-x}Eu_xO_{3-\delta}$. The almost same tendency with those of $BaCe_{1-x}Y_xO_{3-\delta}$ and $BaCe_{1-x}Yb_xO_{3-\delta}$ was observed, indicating orthorhombic *Pnma* and monoclinic $P2_1/m$ for $0.00 \le x \le 0.10$ and $0.15 \le x \le 0.25$, respectively. $BaCe_{1-x}Sm_xO_{3-\delta}$ also shows the same variation of crystal structure as depicted in Fig. 1(c), however, the phase boundary of orthorhombic *Pnma* and monoclinic $P2_1/m$ was observed between $x = 0.15$ and 0.20, which was little higher than those of $BaCe_{1-x}Y_xO_{3-\delta}$, $BaCe_{1-x}Yb_xO_{3-\delta}$ and $BaCe_{1-x}Eu_xO_{3-\delta}$.

On the contrary, the crystal structure of $BaCe_{1-x}Nd_xO_{3-\delta}$ shows different behaviour from other $BaCe_{1-x}RE_xO_{3-\delta}$ as shown in Fig. 1(d). The XRD patterns of $BaCe_{1-x}Nd_xO_{3-\delta}$ with x less than 0.25 were identified as orthorhombic *Pnma* without peak splitting observed for monoclinic $BaCe_{1-x}RE_xO_{3-\delta}$. The peaks with $h + k + l = $ odd