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Magnesium ion distribution and defect concentrations of MgO-doped lanthanum silicate oxyapatite

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ABSTRACT

The distribution of magnesium ions at the lanthanum and silicon sites in MgO-doped lanthanum silicate oxyapatite as well as the concentration of neutral lanthanum vacancies were determined using densities and chemical compositions of the doped samples. On the basis of the density data, it was found that magnesium ions are substituted at the silicon site as well as the lanthanum sites in the oxyapatite phase. Owing to the existence of neutral lanthanum vacancies, it was difficult to evaluate the number of the oxygen ions present, which are related to the oxygen ion conductivity of the compound, from the chemical compositions of the samples alone. Further, it was found that the fact that the total conductivity of MgO-doped lanthanum silicate oxyapatite depends on the MgO concentration as well as that of other defects could not be explained on the basis of conventional defect chemistry.

1. Introduction

1.1. General introduction

Since the discovery of the high oxygen ion conductivity of lanthanoid silicate oxyapatites by Nakayama et al. [1–3], the lanthanoid silicates have used extensively as a solid electrolyte in solid oxide fuel cells and chemical sensors [4,5]. Yoshioka has attempted to improve its oxygen ion conductivity through chemical doping and has reported that magnesium is effective in increasing the oxygen ion conductivity of lanthanum silicate oxyapatite [6–8]. Other researchers have found that two more sites where magnesium ions can be substituted should exist in lanthanum silicate oxyapatite [6–14]. Finally, although several concepts for describing the molecular formulae of MgO-doped lanthanum silicate oxyapatite have been proposed [6–14], there has been no discussion on which concept is adequate for describing actual oxyapatite solid solution.

In previous studies, we had elucidated the chemical compositional region of single-phase MgO-doped lanthanum silicate oxyapatite from the phase diagram of the quasi-ternary $LaO_{1.5}$–SiO_2–MgO system [15,16]. However, the molecular formulae of MgO-doped lanthanum silicate oxyapatite were impossible to determine from only its chemical compositions. The reason is that an extra degree of freedom exists in the compound owing to the existence of neutral lanthanum vacancies ($V_{La}^{\times}$). These abnormal defects are formed owing to the difference between the crystallographic stoichiometry ($La_{10}(SiO_4)_6O_2$) and the stoichiometry by the charge neutrality ($La_{9.33}[V_{La}^{\times}]_{0.67}(SiO_4)_6O_2$), where $V_{La}^{\times}$ is a neutral lanthanum vacancy at the lanthanum sites as the quasi-chemical species. For the lanthanum silicate phase in a quasi-ternary system, the relationship between the chemical composition and the $V_{La}^{\times}$ concentration is not yet known.

The molecular formulae of MgO-doped lanthanum silicate oxyapatite can be determined by measuring its material density. In this paper, we discuss the molecular formulae of MgO-doped lanthanum silicate oxyapatite on the basis of its density and chemical compositions.

1.2. Ambiguity regarding molecular formulae of oxyapatite solid solution in the $LaO_{1.5}$–MgO–SiO_2 system

The ambiguity regarding the molecular formula of MgO-doped lanthanum silicate oxyapatite arises because the compound can be described as two different standard states. On the basis of the crystal structure of lanthanum silicate oxyapatite, the molecular formula of the perfect state can be said to be $La_{10}(SiO_4)_6O_2$. When one considers the valence numbers of the lanthanum ion (+3), the silicon ion (+4), and the oxygen ion (−2), the molecular formula $La_{10}(SiO_4)_6O_2$ does not fulfill the requirement of charge neutrality. Assuming that charge neutrality is determined by the oxygen stoichiometry, the standard molecular formula can be expressed as $La_{9.33}[V_{La}^{\times}]_{0.67}(SiO_4)_6O_2$. On the other hand, if charge neutrality is achieved by completely fulfilling the lanthanum ion, the standard molecular formula should be $La_{10}(SiO_4)_6O_3$; here one interstitial oxygen ion exists per unit cell. These facts suggest that no perfect state of lanthanum silicate oxyapatite exists in the meaning of conventional defect chemistry.

Four different models have been proposed for describing the molecular formulae of MgO-doped lanthanum silicate oxyapatite. The first model (Model 1) is one in which Mg ions are substituted at the La

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sites, allowing the formation of oxygen ion vacancies and/or interstitial oxygen ions [14]. Using this model, the molecular formula can be expressed as,

$La_{9.33+x}Mg_y(SiO_4)_6O_{2+(3x/2)-(y/2)}$, where $\sim 0.2 \le x \le 0.67, 0 \le y \le 2$, and $\sim 0.2 \le x + y \le 0.67$.

The minimum value of x is still unknown, but seems to be approximately −0.2 [17–19]. The second model (Model 2) is one in which Mg ions are substituted at the Si site, resulting in the formation of oxygen ion vacancies and/or interstitial oxygen ions [6–10]. Using this model, the molecular formula can be expressed as,

$La_{9.33+x}\left(Si_{1-(y/6)}Mg_{(y/6)}O_4\right)_6O_{2+(3x/2)-y}$, where $\sim 0.13 \le x \le 0.67$, and $0 \le y \le 1$.

The third model (Model 3) is one in which Mg ions are substituted at the Si site as well as at the La sites while the oxygen stoichiometry is maintained [11–13]. Using this model, the molecular formula can be expressed as,

$La_{9.33+(-2x+2y)/3}Mg_x\left(Si_{1-(y/6)}Mg_{(y/6)}O_4\right)_6O_2$, where $0 \le x \le 0.67$, and $0 \le y \le 1$.

The last model (Model 4) is one in which Mg ions are substituted at the Si site as well as at the La sites, allowing the formation of oxygen ion vacancies and/or interstitial oxygen ions [13]. Using this model, the molecular formula can be expressed as,

$La_{9.33+x}Mg_y\left(Si_{1-(z/6)}Mg_{(z/6)}O_4\right)_6O_{2+(3x/2)-(y/2)-z}$, where $\sim 0.13 \le x \le 0.67, 0 \le y \le 2$, and $0 \le z \le 1$.

If we consider oxygen nonstoichiometry, Model 1 and Model 2 can be represented by Model 4. Hence, the problem is reduced to determining whether Model 3 or Model 4 is appropriate. The difficulty in analyzing these two models is that the compositional regions for the two models almost overlap as shown in Fig. 1 [15,16].

When considering defect control and ionic conductivity, the critical factor is the number of the oxygen ions, which dictates the oxygen ion conductivity. Oxygen ions related to the oxygen ion conduction are considered to be the oxygen ions at 2a site as well as interstitial sites [20–23]. These are described by the number of oxygen species on the right side in the molecular formulae shown above. This is the number of oxygen species as 2 in the case of Model 3 and $2 + 3x/2 - y/2 - z$ in the case of Model 4. The number of oxygen species is labeled as N_o, hereafter.

Although Mg ions are distributed at both the La and the Si sites in different ratios and given that the concentrations of oxygen ion vacancies are also different and depend on the model employed, the compositional regions of Models 3 and 4 are almost similar. Hence, it is necessary to determine the defect model appropriate for MgO-doped lanthanum silicate oxyapatite. On comparing the molecular formulae of Models 3 and 4, it was found that the material density should highly depend on the model used if the lattice parameter and the chemical composition can be determined.

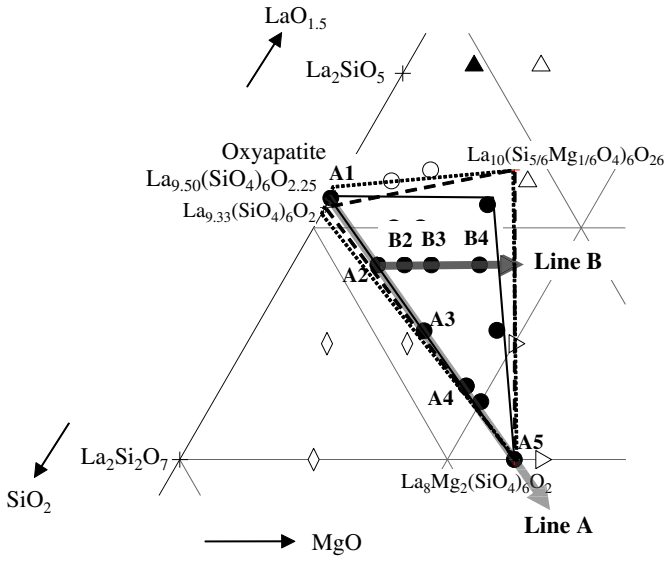

Fig. 1. Partial phase diagram of $LaO_{1.5}$–SiO_2–MgO system at 1773 K [15,16]. The closed circles indicate single-phase oxyapatite. The labels indexed in Tables 1 and 2 were shown around the sample composition points. The broken and dotted lines represented the compositional boundary of Model 3 and Model 4, respectively. Inside of the solid line is the oxyapatite single phase region at 1773 K determined by the experiments.

2. Materials and methods

2.1. Sample preparation

All the samples tested were synthesized by a water-based sol–gel method [15,16,19]. Samples with two series of compositions were used for the density measurements. The first composition series was the solid solution of $La_{9.50}(SiO_4)_6O_2$ and $La_8Mg_2(SiO_4)_6O_2$; this series corresponds to composition line A in Fig. 1. The second series corresponded to composition line B in Fig. 1. This composition line corresponded to the part of SiO_2 that was substituted into MgO at a constant $LaO_{1.5}$ concentration. Powder X-ray diffraction (XRD) patterns of all samples are confirmed as the oxyapatite single phase as shown in Fig. 2(a) and (b) [15,16]. In addition, the single phase formation is consistent from the phase relationships by means of quasi-ternary phase diagram in the $LaO_{1.5}$–SiO_2–MgO system [15,16]. All the sample data related to the density analyses are listed in Tables 1 and 2.

For material density measurements, it is preferable to use porous bulk ceramic in order to prevent errors arising from any existing closed pores. Hence, porous MgO-doped lanthanum silicate oxyapatite ceramics were fabricated using the following procedure. First, the precursor powder was prepared by a previously described method [15]. It was then heated at 1273 K for 3 h in air to remove any residual carbon. This preheated powder was then pulverized using an agate mortar and pestle, and the powder was pressed into 6 to 7 pellets having a diameter of 20 mm and a thickness of 3 mm under a pressure of 63 MPa. The powder at this stage shows high sinterability because the primary particle size is less than 100 nm [24]. Next, well-sintered ceramic disks were obtained by heating the pellets at 1773 K for 6 h in air. One sintered pellet was used for electrical conductivity measurements. The remaining sintered pellets were again crashed into a powder using an alumina mortar and pestle and were then pressed into pellets under a pressure of 63 MPa. The resulting pellets had a diameter of 20 mm and a thickness of approximately 6 mm. Next, porous sintered pellets were obtained by sintering these pellets at 1773 K for 6 h in air. Due to rough granulation by hand using alumina mortar and pestle, the sinterability of the powder becomes bad. As a result, porous sintered pellets were obtained by these procedures. The relative densities of these porous pellets were about 60 to 70% of their theoretically expected values. The lattice parameter of the oxyapatite was calculated from the XRD peaks [15,16]. The porous pellets were broken into fragments using an alumina pestle; the smallest edge of these fragments was less than 7 mm. These fragments were subsequently used for the material density measurements.

2.2. Material density measurements

The material densities of the samples were measured using a glass pycnometer having a volume of 5 ml. 2-Propanol (99.5%, Wako Pure Chemical Industry, Inc., Japan) was used as the saturation solvent. First, the weight of the empty pycnometer was measured. Then, the