Journal of Thermal Analysis and Calorimetry, Vol. 81 (2005) 545–548

WATER UPTAKE AND INFRARED ABSORPTION IN $SrZr_{0.95}M_{0.05}O_{3-\alpha}$ (*M*=Ga, Sc, Y AND Nd)

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Proton concentration in $SrZr_{0.95}M_{0.05}O_{3-\alpha}$ (*M*=Ga, Sc, Y and Nd) was measured with a thermobalance at different temperatures (T=673–973 K) and water vapor pressures (P_{H_2O}=0.9–12.8 kPa). At all the pressures and temperatures examined, the amount of proton concentration in these samples is in the order of Sc>Y>Ga>Nd. By an equilibrium evaluation, we estimated the maximum possible proton concentration about 2.0 mol% in these samples. Infrared (IR) absorption spectra are measured in these samples. The absorption bands can be fitted by four (*M*=Ga, Y, Nd) or three (*M*=Sc) Gaussian bands.

Keywords: *proton concentration, proton conductor,* $SrZrO_3$

Introduction

Oxygen-deficient perovskite oxides are oxide ion conductors in a dry environment. In a humid atmosphere, however, some of them absorb water to fill up oxygen vacancies, release mobile protons into the structure, and thereby become proton conductors [1, 2]. Among them zirconate-based ceramics, $SrZr_{1-x}Y_xO_{3-\alpha}$ for example, have high chemical stability as well as high proton conductivity so that they are expected to be applied to fuel cells and chemical pumps.

The water uptake into and release from these materials can be described as follows [3].

$$H_2O+V_o^{\cdot\cdot}\xleftrightarrow{K_1}2H^{\cdot}+O_o^{x} \tag{1}$$

In equilibrium, proton concentration $[H^{\cdot}]$ should be given by

$$[H^{\cdot}]=\frac{K_1P_{H_2O}}{4}\left[\sqrt{1+\frac{8\times[M']}{K_1P_{H_2O}}}-1\right] \tag{2}$$

where $[M']$ is trivalent dopant concentration, P_{H_2O} partial pressure of water vapor, and K_1 equilibrium constant. According to this equation, $[H^{\cdot}]$ increases in proportion to $P_{H_2O}^{1/2}$ at low P_{H_2O} and asymptotically approaches $[M']$ at high P_{H_2O}. However, there have been some arguments about whether Eq. (2) is strictly obeyed or not.

Yajima *et al*. [4] measured proton concentration in $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ as a function of water vapor pressure (0.7–3.8 kPa) at various temperatures (873–1273 K). They found that at 873 K, for example, the proton concentration increased up to 4.0 mol% with increasing pressure and concluded that Eq. (2) holded in their experiment. On the other hand, Krug *et al.* [5] measured proton concentration in $SrZr_{0.95}Yb_{0.05}O_{3-\alpha}$ at 0.6–4.0 kPa and 673–1073 K. They obtained, however, much lower proton concentration. At 873 K and 4.0 kPa, for example, the proton concentration in $SrZr_{0.95}Yb_{0.05}O_{3-\alpha}$ was only 0.95 mol% in their experiment. Actually, Krug *et al*. [5, 6] were able to reproduce the observed pressure dependence by using a modified version of Eq. (2), in which $[M']$ was not a nominal dopant concentration but a kind of fitting parameter. (They referred to the dopant concentration thus determined as 'effective' dopant concentration.) The 'effective' dopant concentration or the maximum possible concentration of protons was determined to be 1.89 mol%, which is considerably less than the nominal dopant concentration of 5.0 mol%.

In the present study we measure the proton concentration in $SrZr_{0.95}M_{0.05}O_{3-\alpha}$ (*M*=Ga, Sc, Y or Nd) up to higher water vapor pressure than ever. A purpose is to evaluate more accurately the 'effective' dopant concentration or the maximum possible concentration of protons. Another purpose is to discuss the difference in proton concentration due to the difference in trivalent dopant cations. We also measure infrared (IR) absorption spectra of OH-stretching mode for these samples.

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1388–6150/$20.00

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Experimental

The samples of $SrZr_{0.95}M_{0.05}O_{3-\alpha}$ (*M*=Ga, Sc, Y and Nd) were prepared by solid state reaction of $SrCO_3$, ZrO_2, Ga_2O_3, Sc_2O_3, Y_2O_3 and Nd_2O_3 powders (nominally 99.99% pure, Rare Metallic, Japan).

These raw materials were mixed and pressed into pellets, and then the pellets were calcined at 1623 K for 72 h in air. The obtained materials were ground and pressed into pellets again. The pellets were finally sintered at 1673 K for 24 h in air. X-ray diffraction (RINT2200, Rigaku, Japan) indicated that they consisted of a single perovskite phase.

The proton concentration was determined with a thermobalance which was designed to measure the mass change in water vapor atmosphere up to 20 kPa (equilibrium vapor pressure of water at 330 K). Powdered samples of 10 g were loaded in the thermobalance and heated at 1073 K in dry argon flow before the measurement to remove absorbed water. Then oxygen saturated with water vapor (0.9, 1.3, 2.4, 4.4 or 12.8 kPa) was fed into the thermobalance at selected temperatures (673, 773 or 873 K). The proton concentration was calculated assuming that the change in the sample mass was solely due to the reaction (1).

The samples saturated with water vapor at 673 K were quenched to room temperature in dry O_2. Then their infrared absorption was measured by diffusive reflection with a Fourier transform infrared spectrometer (FT-610, JASCO Corporation) in dry N_2 at room temperature.

Results and discussion

Confirmation of proton concentration

Figure 1 shows the dependence of proton concentration in $SrZr_{0.95}M_{0.05}O_{3-\alpha}$ (*M*=Ga, Sc, Y and Nd) on partial pressure of water vapor. The proton concentration increases with increase in partial pressure and decrease in temperature. Similar behavior has been observed for $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ [4] and $SrZr_{0.95}Yb_{0.05}O_{3-\alpha}$ [5]. From the data in Fig. 1, we evaluated the 'effective' dopant concentration using the same procedure as Krug's [5, 6]. The obtained values are 2.0, 2.3, 1.9 and 1.9 mol% for Ga-, Sc-, Y-, Nd-doped samples, respectively. They are within the margin of error and indicate that the maximum possible concentration of protons is almost independent of the dopant cations in spite of the large differences in the proton concentration observed. The lines in Fig. 1 are the theoretical ones calculated with these 'effective' dopant concentrations. There is reasonable agreement between the lines and the measurements. The 'effective' dopant concentration of these samples (2.1±0.2 mol%) is comparable to that of $SrZr_{0.95}Yb_{0.05}O_{3-\alpha}$ [5] (1.89 mol%) and is much lower than that of $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ [4, 5] (4.20 mol%).

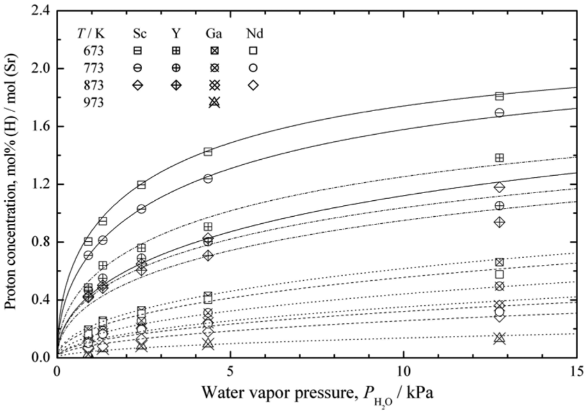

Fig. 1 The dependence of proton concentration on partial pressure of water vapor. Symbols are the observed values. The solid lines, dash-dotted lines, dotted lines, and dashed lines in Fig. 1 are the theoretical ones calculated with the 'effective' dopant concentration of Sc, Y, Ga and Nd, respectively

Figure 2 shows the relation between proton concentration and ionic radii of dopant. At all the pressures and temperatures examined, the amount of proton concentration in these samples is in order of Sc(74.5 pm)>Y(90 pm)>Ga(62 pm)>Nd(98.3 pm). Here, the ionic radii are shown in parentheses. In other words, the sample doped with Sc^{3+}, the ionic radius of which is closest to that of Zr^{4+}, dissolves the largest amount of protons. A possible reason is the distribution of the dopants over two kinds of sites. Müller [7] pointed out the possibility that some of the trivalent dopant cations occupy not Zr sites but Sr sites, resulting in significantly lower proton concentration than dopant concentration. In the present

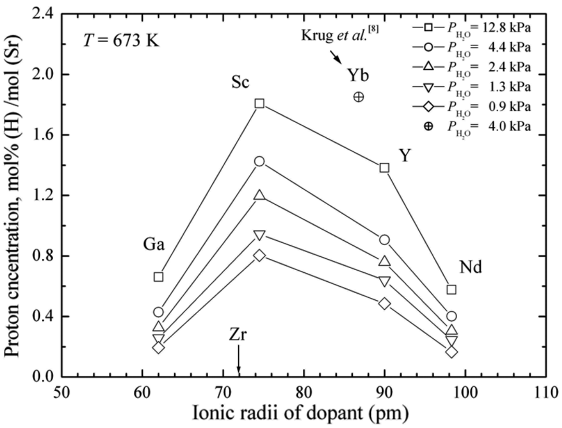

Fig. 2 The dependence of proton concentration on ionic radii of dopant. The Sc doped samples dissolves more water vapor than the other samples

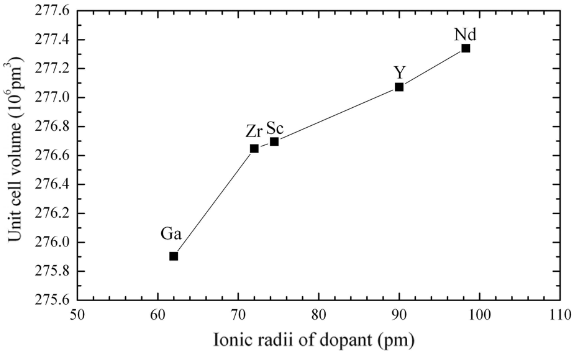

Fig. 3 The dependence of unit cell volume on the kind of dopant cations

study, Sc^{3+} may substitute more Zr^{4+} than the other dopants do. Another possible reason is the distortion of the lattice.

Figure 3 shows the relation between the unit cell volume and the ionic radius of dopant cations. The samples doped with cations larger than Zr^{4+} have larger cell volumes than the undoped one and vice versa. In addition, the cell volume increases with the ionic radius of dopant cations. These results suggest that the dopant cations mainly occupy the Zr sites. If dopant cations were distributed over the two kinds of sites, the distribution should depend on the ionic radius of dopant cations and therefore the maximum possible concentration of protons would also depend on the dopant cations.

Krug *et al*. [5, 6] and Schilling [8] have derived the universal relation of the water uptake process in

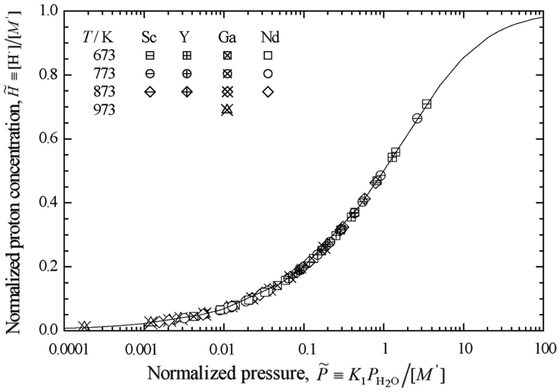

Fig. 4 Normalized proton concentration *vs.* normalized pressure. The dopant concentrations substitute ‘effective’ dopant concentrations

terms of a normalized proton concentration and a normalized water vapor pressure. The relation is expressed as

$$\tilde{H}=\frac{\tilde{P}}{4}\left(\sqrt{1+\frac{8}{\tilde{P}}}-1\right) \qquad (3)$$

where $\tilde{P}$ and $\tilde{H}$ are defined as follows,

$$\tilde{P}\equiv K_1P_{H_2O}/[M']\equiv P_{H_2O}/P^{*}{}_{H_2O}$$

$$\tilde{H}\equiv[H^{\cdot}]/[M']$$

In Fig. 4, we plot all the data in the present experiment together with the theoretical curve given by Eq.

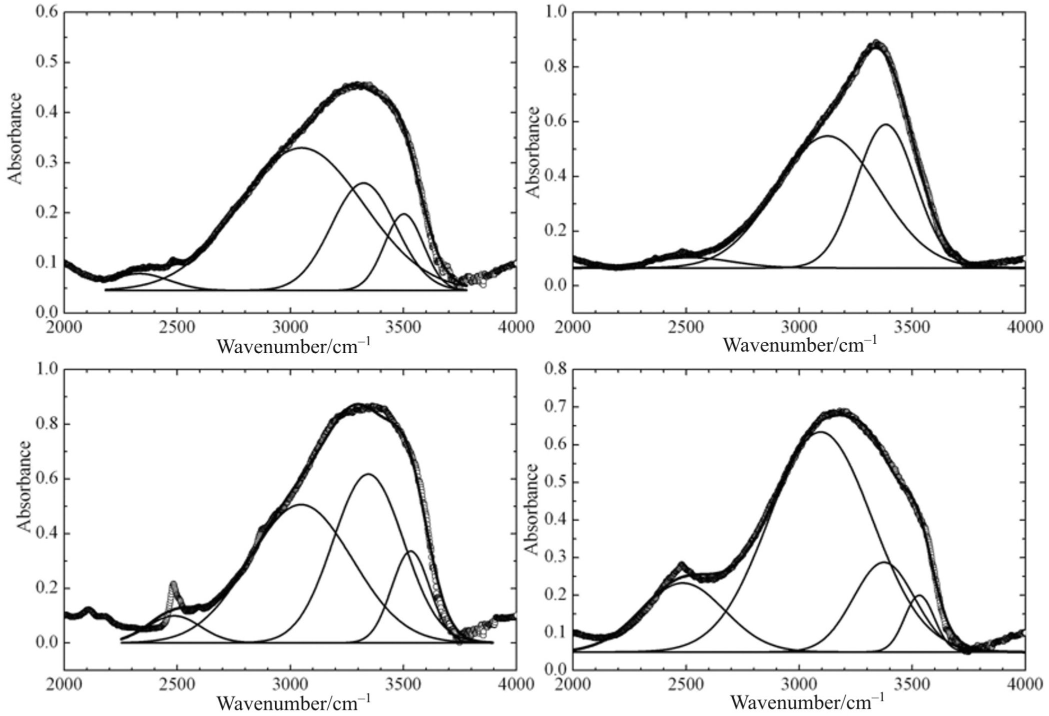

Fig. 5 Infrared absorption spectra of $SrZr_{0.95}M_{0.05}O_{3-\alpha}$ (M=Ga, Sc, Y and Nd) measured at room temperature. These spectra can be well reproduced by Gaussian band A, B, C and D centered at around 2500, 3100, 3400 and 3550, respectively

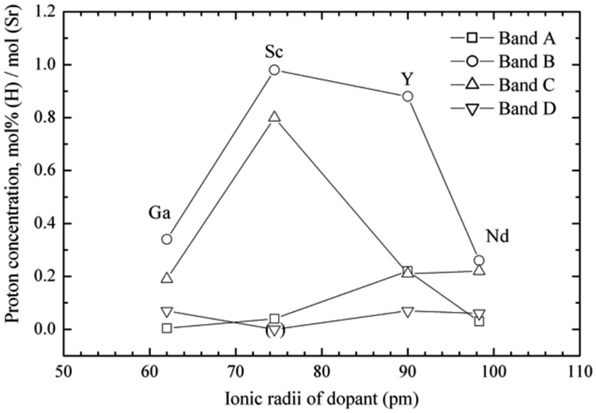

Fig. 6 The proton concentration in each absorption band plotted as a function of ionic radii of dopant cation

(3). As seen from the figure, the universal relation holds in the present experiment as well.

Infrared absorption spectroscopy

The IR absorption spectra of $SrZr_{0.95}M_{0.05}O_{3-\alpha}$ (M=Ga, Sc, Y and Nd) are shown in Fig. 5. The broad absorption bands in the range of 2200–3700 cm^{-1} can be fitted by four (M=Ga, Y, Nd) or three (M=Sc) Gaussian bands. Since each Gaussian band corresponds to particular sites for protons [9], we can estimate the relative contribution of each site to proton uptake from the area of the corresponding band if we assume the absorption coefficient common with all the four bands. Figure 6 shows the proton concentration in each site thus determined. It is seen from the figure that the Sc- and Y-doped samples absorb more protons than the other samples primarily because they accommodate more protons in site B.

Conclusions

At all the pressures and temperatures examined, the amount of proton concentration in these samples is in the order of Sc (74.5 pm)>Y (90 pm)>Ga (62 pm)>Nd (98.3 pm). The sample doped with Sc^{3+}, the ionic radius of which is closest to that of Zr^{4+}, dissolves the largest amount of protons. We obtained the 'effective' proton concentration about 2.0 mol% in $SrZr_{0.95}M_{0.05}O_{3-\alpha}$ (M=Ga, Sc, Y and Nd). These 'effective' dopant concentrations are about 40% of the nominal dopant concentration of 5.0 mol%. This result is comparable to the result of Yb doped one [5] (1.90 mol%).

Infrared absorption spectra have been measured on these samples. It is found that the spectra can be fitted by four (M=Ga, Y and Nd) or three (M=Sc) Gaussian bands. The Sc-doped and Y-doped samples absorb more protons than the other samples primarily because they accommodate more protons in site B.

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DOI: 10.1007/s10973-005-7078-9