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Heat capacity of $Ce_{0.8}Y_{0.2}O_{1.9}$ and the effects of dissolution of water/hydrogen

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Abstract

The heat capacity of polycrystalline $Ce_{0.8}Y_{0.2}O_{1.9}$ and of its water/hydrogen-dissolved sample was measured from 6 to 300 K using an adiabatic calorimeter. The heat capacity of the water/hydrogen-dissolved sample is larger than that of the dry sample below 50 K, and the difference is about 10% at 10 K. Such a difference should originate in the change of lattice vibration spectra caused by the introduction of water/hydrogen. The mechanism is discussed in terms of the defect structure.

Keywords: $Ce_{0.8}Y_{0.2}O_{1.9}$; Heat capacity; Defect structure; Water/hydrogen dissolution

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1. Introduction

Yttria-stabilized zirconia has long been considered to be the best potential candidate as electrolyte for solid oxide fuel cells. Such a use, however, requires rather high temperature of around 1000 °C. Recently rare-earth doped ceria has been investigated vigorously as an alternative to yttria-stabilized zirconia [1,2], as these compounds are expected to have higher ionic conductivity at lower temperatures of about 800 °C. In the rare-earth doped ceria, a possibility of proton conduction has been suggested [3], and recently its higher water/hydrogen dissolution than yttria-stabilized zirconia has been found [4]. If proton conductivity becomes higher, lower temperature operation should be possible. Hydrogen dissolution in oxide ceramics has been evaluated by secondary ion mass spectroscopy for a sample annealed in D_2O atmosphere at 880 and 990 °C [4]. It was found to increase dramatically with increasing rare-earth doping. The hydrogen dissolution in CeO_2 is similar to that in yttria-stabilized zirconia, and the solubility in $Ce_{0.8}M_{0.2}O_{1.9}$ (M = Y, La, Nd, Sm, Gd, Yb) is 10–100 times higher than that in CeO_2 [4]. The mechanism of dissolution should be investigated for electrolyte and electrode functions of rare-earth doped ceria. However, structural properties of the compounds, especially the defect structure, have not been clarified yet. In this study, the effects of the water/hydrogen dissolution on the lattice vibration property have been studied by low temperature heat capacity measurements.

2. Experimental

Polycrystalline $Ce_{0.8}Y_{0.2}O_{1.9}$ was synthesized by a co-precipitation method [5]. $Ce(NO_3)_3 \cdot 6H_2O$ (Wako Pure Chemical Industries Ltd., 99.9% purity) and $Y(NO_3)_3 \cdot 6H_2O$ (Wako, 99.9% purity) were weighed and dissolved into water. The solution was dropped into dilute oxalic acid of pH 6–7. The precipitate was filtered and washed with water and then with ethanol. The powder was dried at 50 °C for 20 h, and calcined at 700 °C for 1 h in air. The sample was pressed into pellets and sintered at 1500 °C for 4 h in air. The dry sample

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was prepared by heating the specimen at 900 °C in vacuum. The wet sample was prepared by annealing the sample under a water of partial pressure of 3 kPa at temperatures from 700 to 900 °C. The dissolution of water was estimated as 0.2 mol% by weighing the wet sample, which meant that the solubility of hydrogen was 0.4 mol%. This value agrees with previous results determined by secondary ion mass spectroscopy [4].

The dry and wet samples were characterized by powder X-ray diffraction experiments using the synchrotron radiation facility at SPring-8 in Japan. The heat capacity was measured from 6 to 300 K using a home-made adiabatic calorimeter. For the heat capacity measurements, a powdered sample of about 6 g was loaded into the calorimeter vessel (gold-plated copper), which was evacuated and then sealed after adding a small amount of helium gas (5 kPa at room temperature) for the sake of thermal uniformity within the calorimeter vessel. The temperature was measured with a rhodium-iron resistance thermometer (Tinsley, 5187U) calibrated at NPL (UK) and Oxford Instruments Ltd. on the basis of ITS-90. The adiabatic control system gives the temperature stability of the calorimeter vessel within 0.00001 K min^{-1}. The performance of the calorimeter was confirmed by measuring the standard reference material SRM 720 (synthetic sapphire) provided by NIST (USA), which indicated an accuracy of the heat capacity value of 0.1% at 100 K. The precision of the data was better than 0.05%. The heat capacity of the sample was obtained by subtracting that of the calorimeter vessel from the measured total heat capacity. The details of the method of the measurements have been described elsewhere [6–8].

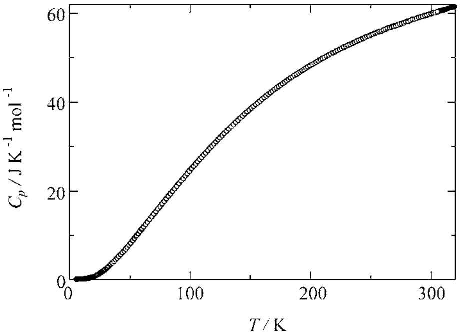

Fig. 1. Measured molar heat capacity of dry and wet $Ce_{0.8}Y_{0.2}O_{1.9}$: (○) dry $Ce_{0.8}Y_{0.2}O_{1.9}$; (●) wet $Ce_{0.8}Y_{0.2}O_{1.9}$.

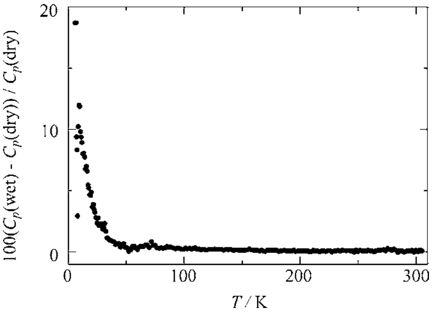

Fig. 2. Heat capacity difference between wet $Ce_{0.8}Y_{0.2}O_{1.9}$ (C_p(wet)) and dry $Ce_{0.8}Y_{0.2}O_{1.9}$ (C_p(dry)).

3. Results and discussion

Fig. 1 shows the measured molar heat capacity, without curvature corrections, for the dry and wet samples of $Ce_{0.8}Y_{0.2}O_{1.9}$. The difference in the heat capacity value of the samples is too small to distinguish each other in this scale. The heat capacity values of the dry sample are tabulated in Table 1. The temperature increment of each measurement is about 2 K. After each heat input, thermal equilibrium of the whole calorimeter vessel including the sample was attained in a few minutes below 20 K and in about 10 min above 100 K. No abnormal relaxation or hysteresis phenomenon was observed for both samples during the experiments. The heat capacity difference is shown in Fig. 2. Above 50 K, the heat capacity of both samples agrees very well within 0.5%. Below 50 K, however, the heat capacity of the wet sample is larger than that of the dry sample by about 10% at 10 K. The difference is small, but the excess heat capacity of the wet sample over the dry sample is clearly apparent below about 200 K. Above 200 K, the difference is within experimental error. A Schottky-type heat capacity equation can be fitted to the excess heat capacity

$$C_{\text{Sch}} = C_{\text{Sch1}} + C_{\text{Sch2}} = 0.004R\left(\frac{\delta_1}{T}\right)\frac{\exp(\delta_1/T)}{[1+\exp(\delta_1/T)]^2} + 0.004R\left(\frac{\delta_2}{T}\right)\frac{\exp(\delta_2/T)}{[1+\exp(\delta_2/T)]^2},$$

where the constant 0.004 is the amount of hydrogen included in the wet sample (Fig. 3). R is gas constant, and $\delta_1 = 300$ K and $\delta_2 = 80$ K are the energy gaps of the two-level systems. Such a good fitting indicates that two independent excitation processes with energies corresponding to 80 and 300 K should be formed in the wet sample as a result of hydrogen dissolvation. It might be related to the tunnelling motion of hydrogen, order-disorder process of the orientation of OH

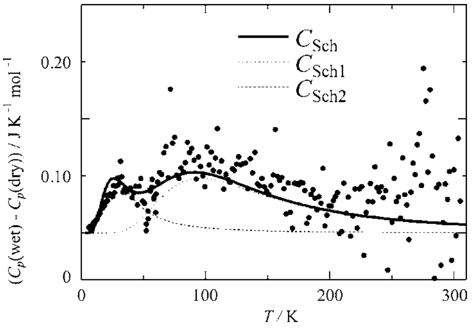

Fig. 3. Heat capacity difference between wet $Ce_{0.8}Y_{0.2}O_{1.9}$ (C_p(wet)) and dry $Ce_{0.8}Y_{0.2}O_{1.9}$ (C_p(dry)). Solid line denotes the results of fitting with two Schottky-two-level systems with energy gap of 300 and 80 K. The dotted and broken lines denote the contribution of Schottky-type heat capacity of two-level system with energy of 300 and 80 K, respectively.

Table 1
Measured molar heat capacity of dry $Ce_{0.8}Y_{0.2}O_{1.9}$

T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})
Series 1		116.72	29.49	186.86	45.90
51.75	8.448	118.44	29.99	188.47	46.19
52.65	8.783	120.15	30.49	190.08	46.48
53.89	9.202	121.83	30.96	191.68	46.75
55.45	9.725	123.50	31.43	193.27	47.03
57.06	10.28	125.19	31.89	194.86	47.27
58.66	10.82	126.90	32.35	196.44	47.58
60.19	11.34	128.65	32.83	198.09	47.84
61.73	11.83	130.53	33.33	199.80	48.11
63.35	12.38	132.49	33.84	201.51	48.38
64.98	12.94	134.43	34.37	203.21	48.65
66.67	13.50	136.35	34.84	204.90	48.92
68.49	14.11	138.25	35.34	206.59	49.18
70.28	14.75	140.14	35.81	208.27	49.48
72.02	15.26	142.01	36.30	209.95	49.73
73.71	15.87	143.87	36.77	211.70	49.95
75.35	16.42	145.72	37.21	213.52	50.25
77.06	17.02	147.55	37.66	215.33	50.50
78.83	17.61	149.36	38.10	217.13	50.80
80.55	18.17	151.17	38.53	218.93	51.04
82.27	18.74	152.96	38.94	220.72	51.27
84.02	19.31	154.75	39.34	222.51	51.55
85.76	19.86	156.52	39.70	224.29	51.76
87.47	20.43	158.28	40.14	226.06	52.00
89.24	21.00	160.03	40.53	227.84	52.30
91.08	21.61	161.77	40.91	229.61	52.49
92.88	22.20	163.50	41.29	231.37	52.72
94.65	22.74	165.22	41.68	233.13	52.93
96.38	23.30	166.93	42.02	234.89	53.17
98.09	23.85	168.64	42.40	236.64	53.36
99.77	24.38	170.33	42.76	238.39	53.59
101.48	24.88	172.02	43.06	240.13	53.81
103.21	25.43	173.70	43.40	241.87	54.02
104.92	25.94	175.37	43.73	243.60	54.23
106.60	26.47	177.03	44.05	245.33	54.43
108.26	26.96	178.69	44.37	247.05	54.70
109.90	27.43	180.34	44.70	248.77	54.79
111.52	27.95	181.98	45.03	250.48	55.05
113.22	28.45	183.61	45.33	252.19	55.21
114.98	28.99	185.24	45.61	253.90	55.42
255.60	55.60	Series 2		24.35	1.155
257.30	55.80	5.81	0.027	25.30	1.311
259.00	55.93	6.51	0.020	26.17	1.453
260.69	56.15	7.06	0.023	26.96	1.610
262.38	56.33	5.78	0.015	27.70	1.756
264.06	56.54	6.42	0.020	28.47	1.910
265.74	56.67	7.05	0.024	29.27	2.070
267.42	56.81	7.56	0.031	30.14	2.270
269.10	56.99	7.99	0.036	31.05	2.470
270.77	57.13	8.46	0.044	31.91	2.660
272.43	57.28	9.11	0.049	32.83	2.895
274.10	57.49	9.81	0.058	33.81	3.155
275.81	57.55	10.39	0.068	34.82	3.414
277.59	57.75	11.04	0.082	35.86	3.691
279.36	57.97	11.73	0.098	37.09	4.025
281.13	58.07	12.33	0.115	38.49	4.415
282.89	58.29	13.08	0.138	39.79	4.782
284.66	58.55	13.94	0.169	41.16	5.185
286.41	58.63	14.68	0.200	42.60	5.597
288.16	58.78	15.34	0.233	44.04	6.012
289.91	59.00	16.07	0.272	45.50	6.451
291.65	59.12	16.88	0.321	46.86	6.834

Table 1 (*Continued*)

T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})
293.38	59.23	17.59	0.374	48.15	7.231
295.11	59.39	18.24	0.423	49.54	7.705
296.83	59.51	18.96	0.485	51.03	8.209
298.56	59.74	19.74	0.557	52.62	8.777
300.28	59.80	20.53	0.637	54.28	9.346
302.01	60.00	21.33	0.735	55.87	9.871
303.72	60.05	22.06	0.823	57.37	10.38
305.44	60.24	22.73	0.914	58.89	10.89
23.45	1.017	60.40	11.39		

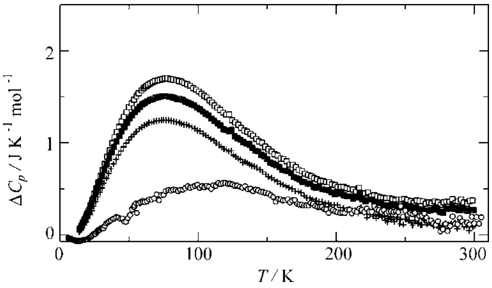

Fig. 4. Excess heat capacity of dry $Ce_{0.8}Y_{0.2}O_{1.9}$ and yttria-stabilized zirconia compared with their calculated values on the basis of additivity rule: (◯) dry $Ce_{0.8}Y_{0.2}O_{1.9}$; (□) $Zr_{0.85}Y_{0.15}O_{1.925}$; (■) $Zr_{0.82}Y_{0.18}O_{1.91}$; (+) $Zr_{0.80}Y_{0.20}O_{1.90}$.

groups formed in the crystal, softening of the lattice vibrations, and so on.

The heat capacity values of dry sample $Ce_{0.8}Y_{0.2}O_{1.9}$ can be compared with those of pure ceria [9] and pure yttria [10]. In previous studies on yttria-stabilized zirconia $Zr_{1-x}Y_xO_{2-x/2}$ [11–13], we analyzed the heat capacity on the basis of additivity rule as follows:

$$C_{p,\mathrm{m}}(\mathrm{calc}) = xC_{p,\mathrm{m}}(\mathrm{YO_{1.5}}) + (1-x)C_{p,\mathrm{m}}(\mathrm{ZrO_2}),$$

where $C_{p,\mathrm{m}}(\mathrm{YO_{1.5}})$ and $C_{p,\mathrm{m}}(\mathrm{ZrO_2})$ denote the heat capacity of pure yttria and pure zirconia, respectively. A similar analysis has been carried out in the present study, and the deviation from the simple additivity rule $\{\Delta C_{p,\mathrm{m}} = C_{p,\mathrm{m}} - C_{p,\mathrm{m}}(\mathrm{calc})\}$ calculated. The results are shown in Fig. 4 together with those obtained for the dry yttria-stabilized zirconia system. The measured heat capacity of $Ce_{0.8}Y_{0.2}O_{1.9}$ is larger than the calculated value on the basis of this simple additivity rule. The excess heat capacity has temperature dependence similar to that of yttria-stabilized zirconia, which extends over a wide temperature range, and the shape is very similar to the Schottky anomaly of a two-level system. The maximum temperature of the excess heat capacity of $Ce_{0.8}Y_{0.2}O_{1.9}$ is about 120 K, which is higher than that of yttria-stabilized zirconia (80 K). The Schottky-type heat capacity curve of a two-level system can be described as a difference of two Einstein-type heat capacities with frequencies ν and 2ν:

$$C_{\mathrm{Sch}}(h\nu, T) = C_{\mathrm{Ein}}(h\nu, T) - C_{\mathrm{Ein}}(2h\nu, T),$$

where h is Planck's constant. The right-hand side of the equation means that the vibration modes at $2h\nu$ change into those at $h\nu$, and, thus, that there is the softening of the lattice vibrations. It is well known that the maximum temperature T_{max} in a Schottky-type heat capacity curve is represented by $k_{\mathrm{B}}T_{\mathrm{max}}/h\nu = 0.42$. Thus, the softened frequency ν differs by 6 THz from the excess heat capacity of $Ce_{0.8}Y_{0.2}O_{1.9}$, and the excess heat capacity can be attributed to the softening of lattice vibration modes. In the case of yttria-stabilized zirconia, we must consider the effect of softening from both the stabilization of high-temperature structure and the formation of oxygen defects [14]. In the present case of yttria-stabilized ceria, the crystal structure of pure ceria and $Ce_{0.8}Y_{0.2}O_{1.9}$ is the same with cubic fluorite structure, and the excess heat capacity should be due to only the formation of oxygen defects. Such a difference should lead to the smaller excess heat capacity of the present ceria compared with zirconia.

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