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ENHANCEMENT OF HUMIDITY SENSITIVITY FOR PEROVSKITE-TYPE OXIDES HAVING SEMICONDUCTIVITY

Yasuhiro SHIMIZU,* Muneharu SHIMABUKURO, Hiromichi ARAI,
and Tetsuro SEIYAMA
Department of Materials Science and Technology, Graduate School of
Engineeing Sciences, Kyushu University 39, Kasuga, Fukuoka 816

The humidity sensitivities of $SrSnO_3$ and $BaSnO_3$ were enhanced slightly by means of calcining their hydroxides, which were prepared by a coprecipitation method. The partial substitution of the A site element of the perovskite-type oxides with lanthanum was more useful for the enhancement of the sensitivity. The highest sensitivity was found in $Sr_{0.95}La_{0.05}SnO_3$ among the specimens studied.

There have been many reports about humidity sensors using materials such as electrolytes, organic polymers, and metal oxides. However, these sensors1) are only capable of using at a temperature range between about 0 and 90 °C ; on the other hand, there are still strong demands for a humidity sensor which is available above 100 °C for drying machines and combustion controlling systems. It was found previously that water vapor acts as an electron-donating gas for semiconductive metal oxides.2) Utilizing this character of a water molecule, we attempted to search for semiconductive materials having humidity sensitivities at a temperature range between 300 and 400 °C. In our previous paper,2) it was reported that humidity sensitivities were found in the perovskite-type oxides containing alkaline earth metal ions at the A site elements such as $CaTiO_3$, $CaSnO_3$, $SrTiO_3$, $SrSnO_3$, and their derivatives of 10% lanthanum substituted oxides. In this study, we attempted to enhance the sensitivity of these specimens by changing a sample preparation method and the amount of partial substitution for the A site element of the perovskite-type oxide. Furthermore, relationships between the sensitivity and the amount of adsorbed water determined by the measurement of temperature programmed desorption (TPD) were investigated.

The perovskite-type oxides were prepared by calcining a mixture of titanium oxide, tin oxide, and alkaline earth carbonate in a desired proportion at 1000 - 1200 °C for 2 - 5 h. In order to obtain samples with large surface area, we adopted a calcination of the hydroxide, $SrSn(OH)_6$ or $BaSn(OH)_6$, which had been prepared by a coprecipitation method from dilute $Na_2Sn(OH)_6$ and a $SrCl_2$ or $BaCl_2$ solution.3) The formation of desired perovskite-type oxides was confirmed by X-ray diffraction method. The surface areas of the specimens were measured by BET method using nitrogen gas. Preparation methods of the specimens and measurements of the humidity sensitivity were reported previously.2) The TPD of water molecules was carried out in the same method.4) A certain amount of the oxide sample was placed into the apparatus and preheated at 600 °C in a flowing mixture of 20% oxygen and 80% helium at 40 cm^3 min^{-1} for 1 h. After the preheat, 0.61 kPa water vapor was mixed to the stream and brought into contact with the sample, followed by cooling from 600 °C to room temperature. Then, the TPD of water molecules was carried out upto 600 °C at a heating rate of 9 deg min^{-1} and at 40 cm^3 min^{-1} helium. The amount of desorbed water was calculated from the peak area of the TPD chromatograms.

Table 1. Characteristics of the samples

No.	Sample	Sintering condition		Surface area	Relative density	α
		Temp/°C	Time/h	m^2 g^{-1}	%	
SS-1	$SrSnO_3$[a)]	800	5	15	41	0.25
SS-2	$SrSnO_3$	1100	2	2.9	55	0.20
BS-1	$BaSnO_3$[a)]	800	5	25	43	0.24
BS-2	$BaSnO_3$	1000	5	14.5	61	0.22
ST-1	$SrTiO_3$	1200	2	1.3	56	-0.22
SLS-1	$Sr_{0.95}La_{0.05}SnO_3$	1200	6	0.79	63	0.37
SLS-2	$Sr_{0.9}La_{0.1}SnO_3$	1200	4	0.56	64	0.34

a) Prepared by calcining a (Sr or Ba)$Sn(OH)_6$.

The characteristics of the specimens studied are summarized in Table 1. As shown in Fig. 1, the log-log plots of the conductivity (σ) vs. water vapor pressure (P_{H_2O}/Pa) give straight lines with slopes (α) and can be expressed

$$\sigma = \sigma_1 P_{H_2O}{}^{\alpha} \qquad (1)$$

where σ_1 denotes the conductivity at P_{H_2O} = 1 Pa and α corresponds to the degree of the humidity sensitivity. The α values of the specimens obtained form the log-log plots are also listed in Table 1. It is noticed that the sensitivity is enhanced with an increase in the α value. It was found that the preparation of the perovskite-type oxides were possible at relatively low temperatures such as 800 °C by means of calcination of the hydroxides. The samples prepared at this temperature had relatively large surface areas and their sensitivities are then large. The negative value of α was only found in $SrTiO_3$, suggesting that the conduction mechanism of this specimen was a p-type in this condition as was also confirmed by the measurements of thermo-electromotive force.[2)]

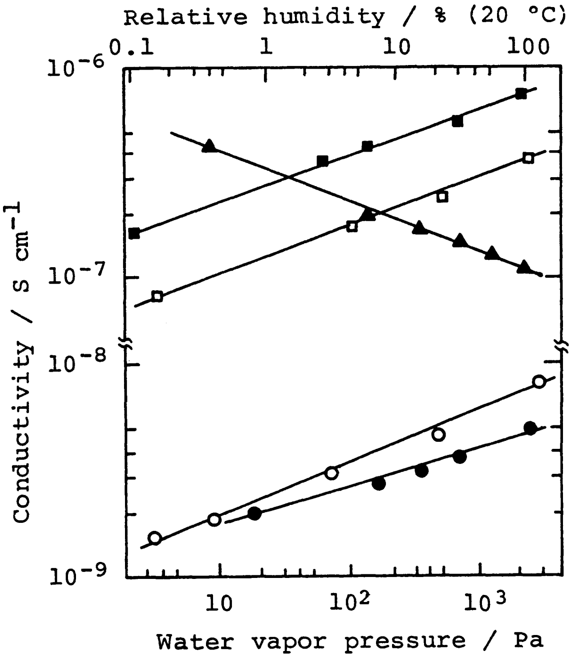

Fig. 1. Conductivity-humidity characteristics of specimens.
○: SS-1, ●: SS-2, □: BS-1
■: BS-2, ▲: ST-1.
Operating temperature ;
SS-1, SS-2, ST-1 = 400 °C
BS-1, BS-2 = 300 °C

The TPD spectra of water molecules from these samples are shown in Fig. 2. It is noticed that the spectra consist of three kinds of desorption peaks with the peak maxima located at 100, 100 - 250, and 300 - 400 °C, which are referred to peak I, peak II, and peak III, respectively. The peak I undoubtedly arises from the desorption of the physisorbed water. The peak II is assigned to molecular water adsorbed on O^{2-} ions through hydrogen bonding. The peak Ⅲ is ascribed to the surface hydroxyls.[4)]

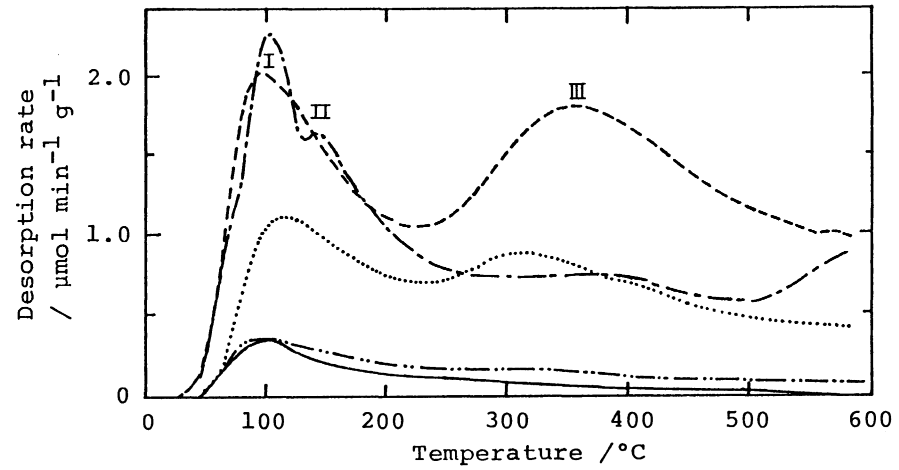

Fig. 2. Temperature programmed desorption spectra of H_2O. —·—: SS-1, —··—: SS-2, ---: BS-1, ·······: BS-2, —: ST-1.

Taking account of both the operating temperature of the conductivity-humidity characteristics and the electron-donating character of a water molecule, the desorption peak Ⅲ is presumed to influence on the sensitivity. Table 2 shows that the maximum temperatures of peak Ⅲ located between 300 and and 350 °C. The amount of desorbed water in a range of 100 deg. below the operating temperature depended markedly on both sample preparation and its composition. It is found by correlating the results of the amount of desorbed water with those on the α value listed in Table 1 that the increment of α value in the same compositions is smaller than that expected for the increase in the amount of desorbed water. For example, the difference between the α value of $SrSnO_3$ (SS-1) prepared by calcining $SrSn(OH)_6$ and that of $SrSnO_3$ (SS-2) prepared by calcining the mixture of tin oxide and strontium carbonate is only 0.05, while the amount of desorbed water, V_d (300 - 400 °C), of SS-1 sample is 4.6 times larger than that of SS-2 sample. On the other hand, it has become apparant from comparison of the results obtained at different compositions that the amount of desorbed water measured by TPD results has no influence on the α value. For example, the absolute value of α for $SrTiO_3$, which gave the smallest amount of desorbed water, was comparable to those of other samples. These results allow us to anticipate that the sensitivity is influenced both by the amount of chemisorbed water and by electronic interactions between chemisorbed water and oxide surface.

The effects of the partial substitution of Sr^{2+} of $SrSnO_3$ with La^{3+} on the conductivity-humidity characteristics were also investigated as shown in Fig. 3. Figure 4 describes the effects of partial substitution of lanthanum on the TPD spectra of water molecules on the desorption rate of water per surface area of the samples. The α values and the amount of desorbed water of these samples are also summarized in Tables 1 and 2, respectively. These

Table 2. Temperature of the peak Ⅲ and H_2O desorption amount from samples

No.	Peak Ⅲ V_d µmol g^{-1}	Peak Ⅲ T_M °C	Amount of desorbed water [a)] V_d(300-400 °C) µmol g^{-1}	Amount of desorbed water [a)] V_d(200-300 °C) µmol g^{-1}
SS-1	20	356	7.9	—
SS-2	5.0	332	1.7	—
BS-1	56	352	—	10
BS-2	25	310	—	5.5
ST-1	1.6	322	0.73	—
SLS-1	0.81	335	0.72	—
SLS-2	2.3	345	1.9	—

V_d : Amount of desorbed water, T_M : maximum temperature of peak Ⅲ, a) Calculated from a desorption peak above peak Ⅲ.

samples show sharp peak III at about 340 °C and the peak enlarges as lanthanum content increase, while only a broad peak is found in $SrSnO_3$. This phenomenon arises from a change of an adsorbed species caused by the partial substitution of lanthanum. The sharp peak III is anticipated to exhibit a strong electronic intereaction with the oxide surface, because $Sr_{0.95}La_{0.05}SnO_3$ (SLS-1) and $Sr_{0.9}La_{0.1}SnO_3$ (SLS-2) have higher α values, compared with that of $SrSnO_3$ (SS-1), in spite of their relatively small amount of desorbed water. The largest α value, 0.37, is found in SLS-1 specimen, among the specimens studied.

In conclusion, the humidity sensitivities of the perovskite-type oxides were enhanced slightly by means of increasing their surface areas. The partial substitution of the A site element of the oxides was more useful for the enhancement of the humidity sensitivities. This large enhancement was considered to result from a strong electronic intereaction between the adosrbed species and the oxides surface.

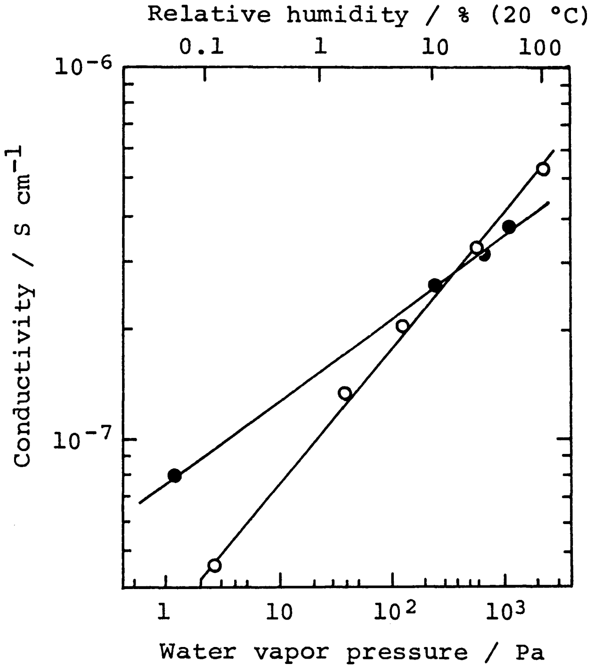

Fig. 3. Effects of the partial substitution on the conductivity-humidity characteristics.
o: SLS-1, ●: SLS-2.

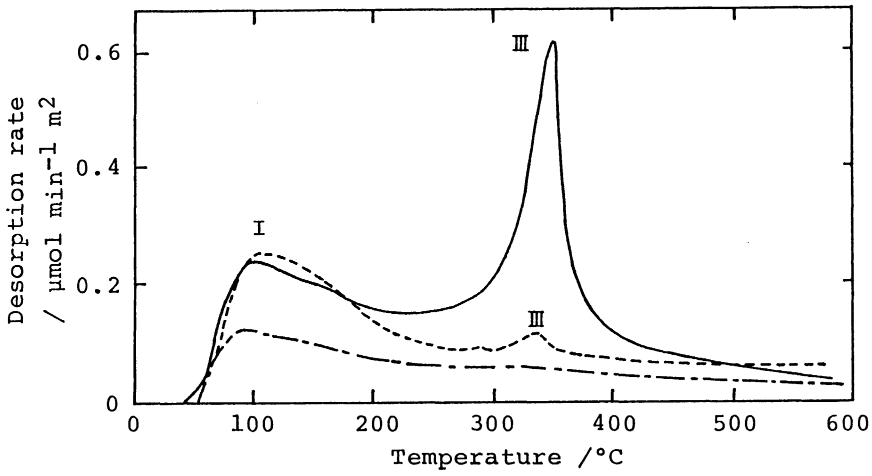

Fig. 4. Temperature programmed desorption spectra of H_2O.
—·—: SS-2, ----: SLS-1, ——: SLS-2.

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