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Control of Temperature Dependence of Intrinsically Humidity-Sensitive Elements

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In lead chromates thick film elements, humidity sensitivity can be controlled by adjusting the proportion of hydrophilic Pb_2CrO_5 to hydrophobic $PbCrO_4$, but temperature dependence can not be controlled. Elements stable against changes in the ambient temperature were found in some combinations of oxide with the host component $PbCrO_4$, as confirmed by the fact that curves of electrical resistance versus relative humidity overlapped at various ambient temperatures from 20°C to 80°C. The effective oxides were SnO_2, V_2O_5 and Fe_2O_3. The most effective amount of oxide was 0.3 mol per mol of $PbCrO_4$. These results suggest that appropriate combinations of oxides can improve the temperature stability of humidity sensitivity. Using a humidity sensor which is stable in the surrounding temperature, the humidity sensor system can be miniaturized and its reliability increased because a temperature compensation circuit is not required.

1. Introduction

Most ceramic humidity sensors are controlled by adjusting the size and distribution of pores. Thus such sensors are called pore-controlled types. For adsorbing water vapor, size and distribution of pores must be controlled. As humidity-sensitive ceramics, some hard-to-sinter oxides are used to produce the appropriate pore size. In this case, the sintering temperature is very high.

Because the intrinsic sensitivity of Pb_2CrO_5 to moisture is utilized in lead chromate humidity sensors, the sintering temperature is no higher than 850°C, which is one of the merits of these systems. Control of composition is possible by combining various oxides with $PbCrO_4$, which is another merit.

The thick film element in lead chromates is different from that normally found in humidity sensors, because capillary action is not utilized for adsorbing water vapor. The vapor adsorption of a lead chromate element is a result of its sensitivity to humidity.(1) We call such a humidity sensor a composition-controlled type or intrinsic type, while a pore-controlled type is typical in ceramic sensors.

The relation between electrical resistance and relative humidity when hydrophilic Pb_2CrO_5 and hydrophobic $PbCrO_4$ are combined is shown in Fig. 1. The sensitivity in the low-humidity region increases as the proportion of Pb_2CrO_5 to $PbCrO_4$ increases. The proportion of Pb_2CrO_5 to $PbCrO_4$ can be changed by combining various oxides with the host material $PbCrO_4$,(2) implying that the element in a lead chromate system is either composition-controlled or intrinsic.

By adjusting the composition of a lead chromate system, other properties besides humidity sensitivity can be controlled. Thus various oxides were examined, and stability against changes in the ambient temperature was obtained for some combinations of certain oxides and $PbCrO_4$. In this study, the temperature dependence of humidity sensitivity was

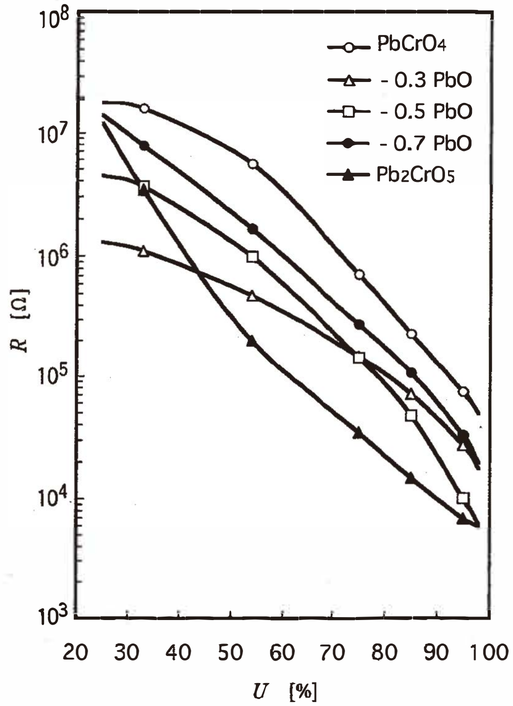


Fig. 1. Humidity-sensitive characteristics of $PbCrO_4$-nPbO element.

examined versus various proportions of Pb_2CrO_5 to $PbCrO_4$ that were prepared by combining PbO with $PbCrO_4$. From the difference in results between the elements composed of lead chromates only and those containing other oxides, the effect on temperature characteristics of combining oxides with $PbCrO_4$ was discussed.

2. Experiment

A schematic of the process for preparing thick film elements is represented in Fig. 2. Host material, 1 mol of $PbCrO_4$, combined with 0.1 ~ 1.0 mol of PbO and 0.001 mol of La_2O_3 was ball-milled. La_2O_3 was added to reduce the electrical resistivity. The mixed powders were dried and pressed into disks 13 mm in diameter and 3 mm thick. The disks were then sintered in air at 650 ~ 750°C for 1 h. Each sintered disk was crushed to a powder and mixed with ethyl cellulose to form a paste. The paste was printed on an Al_2O_3 ceramic plate on which comb-shaped electrodes of Ag-Pd had been formed. The printed films were heat-treated in air at 675°C ~ 750°C for 30 minutes. The electrical resistance of the thick film elements was measured versus various relative humidities. The composition and microstructure of the elements were determined by XRD and EDX, respectively.

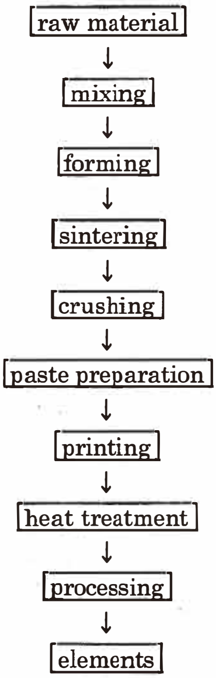


Fig. 2. Flow chart for the manufacture of lead chromate thich film elements.

3. Results

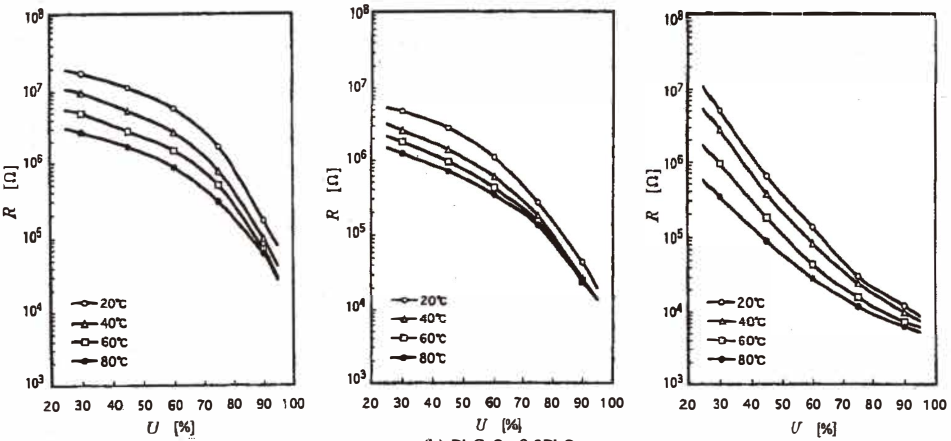
Figure 3 shows the humidity-sensitive characteristics measured at various temperatures in thick film elements of (a) $PbCrO_4$, (b) $PbCrO_4$-0.3PbO and (c) Pb_2CrO_5. The dependence on temperature is strong in all elements. The temperature dependence of $PbCrO_4$-0.3PbO elements tends to decrease in the high-humidity region, as shown in Fig. 3(b).

Figure 4 shows the SEM patterns of thick film elements of (a) $PbCrO_4$, (b) $PbCrO_4$-0.3PbO and (c) Pb_2CrO_5. Minute particles aggregate closely and few pores can be observed. The particle size is 2~ 3 μm in the $PbCrO_4$-0.3PbO element and ~10 μm in both $PbCrO_4$ and Pb_2CrO_5 elements.

Figure 5 shows the X-ray diffraction patterns of thick film elements of (a) $PbCrO_4$, (b) $PbCrO_4$-0.3PbO and (c) Pb_2CrO_5. In the $PbCrO_4$-0.3PbO element, both $PbCrO_4$ and Pb_2CrO_5 coexist.

4. Discussion

Humidity characteristics have been controlled by combining a specific oxide with $PbCrO_4$. Various combinations have been examined in the thick film elements. In the elements of $PbCrO_4$-SnO_2, $PbCrO_4$-V_2O_5, $PbCrO_4$-Fe_2O_3, the temperature dependence of humidity characteristics was found to decrease markedly. The most effective molar ratio of combined oxide was 0.3 in all cases. Figures 6, 7 and 8 show the respective temperature dependences of humidity characteristics in the elements with an oxide molar ratio of 0.3.(3,4)



(a) PbCrO4

(b) PbCrO4-0.3PbO

(c) Pb2CrO5

Fig. 3. Humidity-sensitive characteristics at various temperatures in lead chromate (a) $PbCrO_4$, (b) $PbCrO_4$-0.3PbO and (c) Pb_2CrO_5.

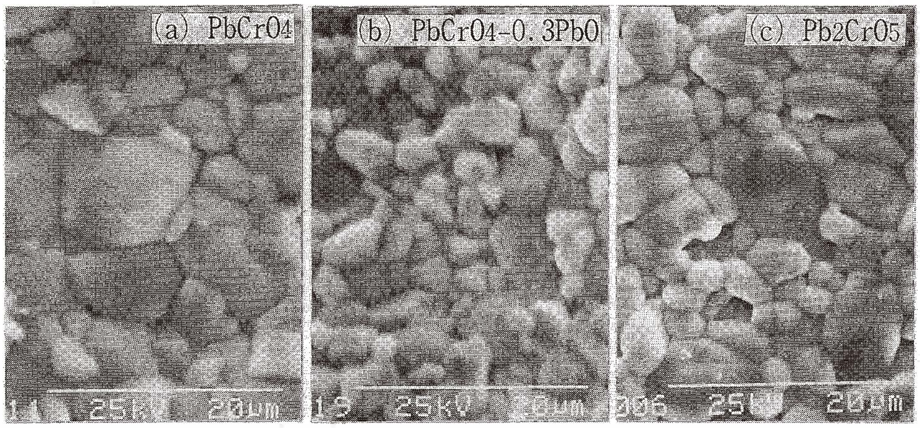


Fig. 4. SEM patterns on the surface of lead chromate systems (a) $PbCrO_4$, (b) $PbCrO_4$-0.3PbO and (c) Pb_2CrO_5.

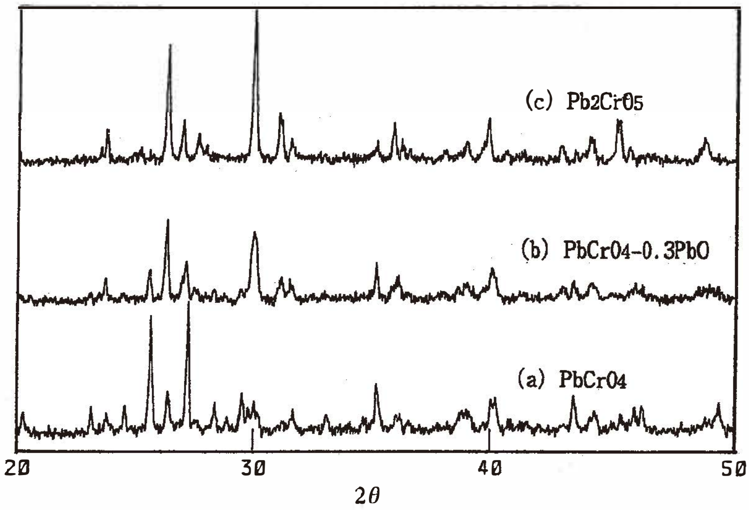


Fig. 5. X-ray patterns of lead chromate system elements.

To establish a method of preparation for an element stabilized against changes in ambient temperature, analysis from the viewpoint of material design is required of the above effects for a combined oxide.

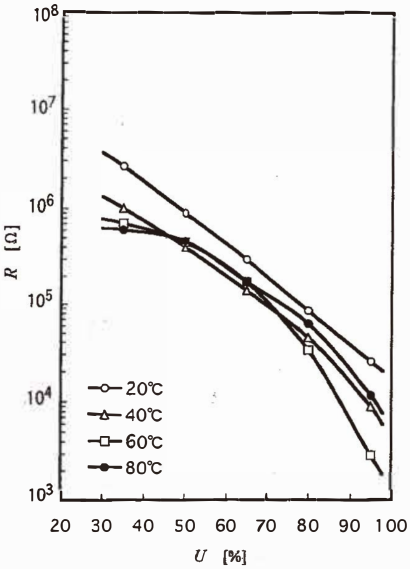


Fig. 6. Humidity-sensitive characteristics at various temperatures for elements containing 0.3 molar ratio of SnO_2.

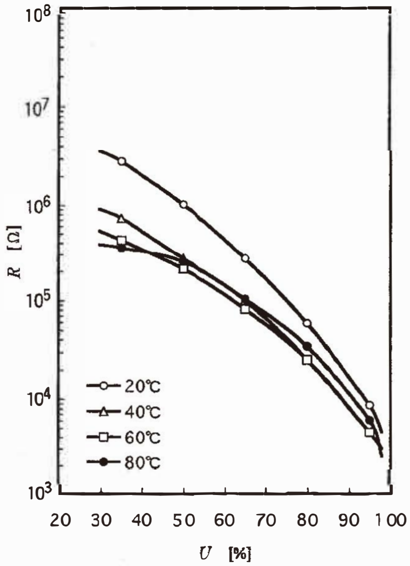


Fig. 7. Humidity-sensitive characteristics at various temperatures for elements containing 0.3 molar ratio of V_2O_5.

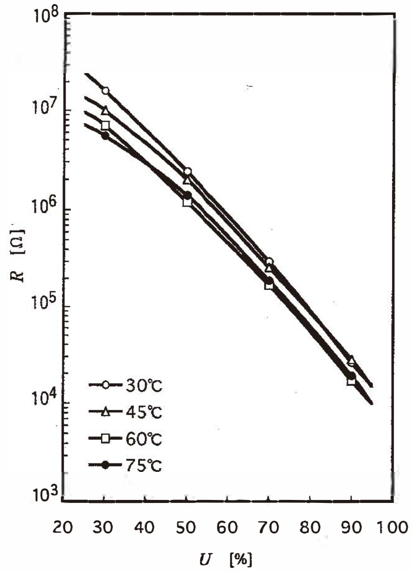


Fig. 8. Humidity-sensitive characteristics at various temperatures for elements containing 0.3 molar ratio of Fe_2O_3.

In these experiments, three thick film elements of $PbCrO_4$, $PbCrO_4$-0.3PbO and Pb_2CrO_5 were studied with respect to the temperature dependence of humidity characteristics. The following results were obtained;

(1) Temperature dependence of humidity characteristics was significant in all three elements.

(2) No small pores were observed on the surface of the three elements.

(3) $PbCrO_4$ and Pb_2CrO_5 coexisted in the $PbCrO_4$-0.3PbO element.

These results suggest that the temperature dependence of humidity characteristics of lead chromates is not caused by the compositional change from $PbCrO_4$ to Pb_2CrO_5 but that combination with an oxide is more effective for decreasing the temperature dependence.

The factors affecting the temperature dependence of humidity characteristics were found to be microstructure, surface conditions and pore distribution. However, the problem of the mechanism of the temperature dependence still remains unsolved.

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