Cu-P-Y-O BASED CERAMIC HUMIDITY SENSOR : SOLID-STATE REACTION BETWEEN Cu$_3$(PO$_4$)$_2$·3H$_2$O AND Y$_2$O$_3$

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Abstract  The solid-state reaction routes to humidity-sensitive Cu-P-Y-O based substances, particularly to YPO$_4$ from Cu$_3$(PO$_4$)$_2$·3H$_2$O and Y$_2$O$_3$ was investigated by XRD, TG-DTA, and SEM. In addition, the sintering temperature of the Cu-P-Y-O based ceramics was correlated with the humidity-sensitive characteristics, and the presence of Cu$_2$O in the excellent Cu-P-Y-O based humidity sensor was also confirmed.

INTRODUCTION

Very recently, we have reported that a Cu-P-Y-O based ceramics (designated as CPY), which was produced by the solid-state reaction between Cu$_3$(PO$_4$)$_2$·3H$_2$O and Y$_2$O$_3$, showed a good humidity-sensitive characteristics; its electric resistance decreased by three orders in magnitude as the surrounding relative humidity increased from 0% to 96%. It has been also found that a typical CPY sample is composed of several crystalline phases such as YPO$_4$, Cu$_2$Y$_2$O$_5$, CuO, and unreacted Y$_2$O$_3$. Among them, YPO$_4$ has been turned out to be a key substance to which the humidity-sensing potential of the CPY element is owing. The solid-state reaction mechanism for producing YPO$_4$, however, has not been revealed. In addition, Cu$_2$O has been presumed to contribute to the humidity-sensitivity of excellent CPY elements in the extremely low humidity range, but the presence of Cu$_2$O has never been confirmed so far. Therefore, those subjects were dealt with in the present paper.

EXPERIMENTAL

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Several Cu-P-Y-O elements listed in Table 1 were prepared as follows. A calculated amount of Cu$_3$(PO$_4$)$_2$·3H$_2$O and Y$_2$O$_3$ was mixed and ground, followed by calcining at an elevated temperature for 5 h in air. The resulting substance was pulverized, pressed at 10000 kg·cm$^{-2}$ into a disk with both 13 mm in diameter and 0.90 mm in thickness and finally sintered at various temperatures for 3 h in air. A BF-type element shown in Fig.1 was made by applying a silver paste onto both faces of a CPY disk and by heating it at 700 °C for 10 min. The electric resistance of a sensor element, which was exposed to a water vapor equilibrated with a saturated salt solution at 25 °C, was measured by so-called four-point resistance measurement method by using a LCR meter (YHP4261A) under the applied voltage of 1 V ac (1 kHz). The TG-DTA analysis of a sample (10 mg) was made with a ULVAC TGD-7000 in the temperature range from 25 °C to 1200 °C. The X-ray diffraction analysis was performed with a Rigaku Rint-1200 (target: CuKα).

RESULTS AND DISCUSSION

Figure 2 shows the results of X-ray analysis of CPY-10 samples heated at 130 °C - 790 °C. After heating at 130 °C, strong diffraction peaks due to unreacted Y$_2$O$_3$ and very weak peaks due to Cu$_3$(PO$_4$)$_2$·3H$_2$O and Cu$_3$(PO$_4$)$_2$ were observed. On heating at 300 °C, the peaks of Cu$_3$(PO$_4$)$_2$·3H$_2$O diminished but those of Cu$_3$(PO$_4$)$_2$ did not change up to 500 °C. When heated at 500 °C, the peaks of Cu$_3$(PO$_4$)$_2$ disappeared and new peaks assigned to Cu(PO$_3$)$_2$ appeared. The latter peaks grew steadily up to 730 °C. At 730 °C Cu(PO$_3$)$_2$ vanished and both Cu$_5$O$_2$(PO$_4$)$_2$ and YPO$_4$ began to form. Cu$_5$O$_2$(PO$_4$)$_2$ disappeared and CuO appeared newly at 790 °C. YPO$_4$ kept on increasing in compensation for decreasing Y$_2$O$_3$ during the temperature was raised up to 950 °C. At 950 °C Y$_2$O$_3$ diminished.
FIGURE 2 The X-ray diffraction patterns of CPY-10 sintered at various temperatures: Δ; Cu₃(PO₄)₂, ○; Y₂O₃, ×; Cu(PO₃)₂, ◊; Cu₅O₂(PO₄)₂, ●; YPO₄, ◇; Cu₂Y₂O₅, □; CuO.
completely, the increase of YPO₄ stopped, and new substance Cu₂Y₂O₅ appeared. At 1050 °C CuO began to change into Cu₂O. Judging from those results, we propose the following scheme.

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\begin{align*}
\text{Cu₃(PO₄)₂·3H₂O} & \rightarrow \text{Cu₃(PO₄)₂} \rightarrow \text{Cu(PO₃)₂} + 2\text{CuO} \\
2\text{Cu(PO₃)₂} + 3\text{CuO} + \text{Y₂O₃} & \xrightarrow{600 \sim 730 ^\circ C} \text{Cu₅O₂(PO₄)₂} + 2\text{YPO₄} \\
\text{Cu₅O₂(PO₄)₂} + \text{Y₂O₃} & \xrightarrow{730 \sim 790 ^\circ C} 5\text{CuO} + 2\text{YPO₄} \\
2\text{CuO} + \text{Y₂O₃} & \xrightarrow{950 ^\circ C} \text{Cu₂Y₂O₅}, 4\text{CuO} \xrightarrow{950 ^\circ C} 2\text{Cu₂O} + \text{O₂}
\end{align*}
\]

**SCHEME**  Reaction routes to YPO₄, Cu₂O, etc.

Figure 3 demonstrates the effect of the sintering temperature of a CPY-10 sample on the humidity-sensitive characteristics. When sintered at 850-1040 °C, the characteristics of a CPY-10 sample was similar to one another. Although the resistivity of a CPY-10 sample sintered at 700 °C or 750 °C was considerably higher than that of a CPY-10 sample sintered at 850-1040 °C, the humidity dependence of resistivity for the former sample was similar to that for the latter sample in the whole humidity range. On the other hand, the CPY-10 sample sintered at 1050 °C lost its humidity-sensitivity, and its resistivity was quite similar to that of Cu₂O, indicating the occurrence of abrupt physical and chemical change to yield Cu₂O.

Figure 4 shows the TG-DTA for a CPY-10 sample. The decrease in weight took place gradually up to 500 °C and became remarkable suddenly around 1050 °C. The latter weight loss seems to be related with the endothermic peak at 1050 °C. As described above, CuO was transformed to Cu₂O at 1050 °C. This reaction successfully explains
the TG-DTA behavior at 1050 °C. The exothermic peak at 790 °C, however, can not be explained at the present stage.

Judging from the reaction paths for producing YPO$_4$ and others, a CPY-5 sample sintered at 950 °C is supposed to contain not only YPO$_4$ and Cu$_2$Y$_2$O$_5$ but considerable amount of unreacted Y$_2$O$_3$, and moreover, a CPY-15 sample sintered at 950 °C is supposed to be composed of YPO$_4$ as well as of a Cu-P-O based composite substance which would be produced from excess Cu$_3$(PO$_4$)$_2$·3H$_2$O in the starting materials. The XRD data shown in Fig.5 gives support to all of the above predictions. The reason Fig.5 gives no information about the Cu-P-O based substance is because such a substance will be amorphous.

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![FIGURE 4 TG and DTA curves of CPY-10 sample. Heating rate: 20 °C/min, atmosphere; air.](image)

![FIGURE 5 The X-ray diffraction patterns of CPY-5 (a) and CPY-15 (b) sintered at 950°C: O : Y$_2$O$_3$, ● : YPO$_4$, ◇ : Cu$_2$Y$_2$O$_5$, □ : CuO.](image)
Figure 6 shows the scanning electron micrographs of several CPY samples. The CPY-5 sample appears to be composed of mainly large particles, whereas the CPY-10 sample looks like an ensemble of nearly homogeneous small particles and moreover, seems to have something like pores. On the other hand, in the CPY-13 sample, grains get still larger and fine particles disappear. In the case of the CPY-15 sample, it appears that the growth of the grains (black parts in the photograph) reaches a spatial limit and so a glassy substance (white parts in the photograph) is pushed out of the grain-boundaries. This glassy substance is thought to be identical to the amorphous Cu-P-O substance described above.

In conclusion, YPO$_4$ has been found to start to form around 730 °C from Y$_2$O$_3$ and at least Cu(PO$_3$)$_2$. In addition, the presence of Cu$_2$O in a CPY-10 sample sintered at 950 °C has been confirmed.

REFERENCES