HUMIDITY-SENSITIVE CHARACTERISTICS OF TITANIUM PHOSPHATES

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Abstract Titanium phosphates $\text{Ti}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ and their derived substances were investigated as humidity-sensitive materials. Among the sensor elements studied, TiP-1-NaOH-800 element which was prepared by immersing $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ in aqueous NaOH solution, followed by calcining at 800 °C, exhibited the best performance from the viewpoint of humidity sensitivity and measurability. Suitable starting materials $\text{Ti}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ and optimum sintering conditions were also investigated.

INTRODUCTION

In recent years, zirconium phosphates have been focused as potential humidity-sensing materials¹⁻³). It is well known that titanium phosphates possess similar surface and structural properties to zirconium phosphates^{4,5}). Therefore, titanium phosphates could also be good humidity-sensitive materials. And indeed, this expectation came true⁶). However, it has not been clarified how the humidity-sensitive characteristics of titanium phosphate sensors depend on both the kind of titanium phosphate and the sintering conditions, and why NaOH-treatment of titanium phosphates resulted in remarkable improvement of the humidity-sensitive characteristics. The humidity-sensitive characteristics of titanium phosphate sensors have never been compared with a commercial sensor so far. The present paper will describe the details of the humidity-sensitive characteristics of both titanium phosphate and NaOH-treated one.

EXPERIMENTAL

Titanium phosphates $\text{Ti}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ and their derived phosphates were prepared as follows: $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (designated as TiP-1) was prepared by heating TiO_2 (4.4 g) in

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85% H_3PO_4 solution (258.2 g) ($\text{P}_2\text{O}_5/\text{TiO}_2$ molar ratio = 20) at 160 °C for 48 h, followed by washing with deionized water, filtrating, and drying at 120 °C for 20 h. $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ (designated as TiP-2) was prepared by Tsuchiko's method⁷). Sodium cation-exchanged titanium phosphate samples were obtained as follows. A powdered as-prepared $\text{Ti}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ (1.0 g) was immersed in 0.1 mol% of NaOH solution (200 ml) at room temperature for 15 h, washed, and calcined at elevated temperatures. Every precalcined sample was pulverized, pressed into a disk with 13 mm in diameter and 0.5-1 mm in thickness. Finally every disk was sintered at 800 °C for 3 h in air.

Structural characterization of powdered samples were carried out by X-Ray diffraction (XRD) technique with a Rigaku 4053 (target: $\text{CuK}\alpha$).

An OS-type element was prepared by printing the comb-pattern electrodes shown in Fig. 1 on the one side of a disk with a silver paste and then by heating at 700 °C for 10 min. A sensor element was placed in a test chamber (200 ml) containing a suitable saturated salt solution (40 ml), which gives a specified relative humidity. The four-point resistance measurements of sensor elements were performed at 25 °C by using a LCR meter (YHP4261A) under an applied voltage of 1 V ac at 1 kHz.

RESULTS AND DISCUSSION

As seen in Fig. 2, the electric resistance dependence of the TiP-1-800 (800: sintering temperature in °C) and TiP-2-800 on relative humidity is quite different. Apparently, TiP-1-800 was better in humidity-sensitive characteristic than TiP-2-800, although they were sintered at the same temperature.

FIGURE 1 Schematic view of OS-type sensor element.

FIGURE 2 Humidity-sensitive characteristics of TiP-1 and TiP-2 sintered at 800 °C

Therefore, TiP-1 was used in the following experiment, unless otherwise stated.

Figure 3 shows the humidity-sensitive characteristics of TiP-1 as a function of sintering temperature. All the resistance values were recorded at steady state, which was attained 1 h after the start of the measurement. TiP-1-400, TiP-1-600, and TiP-1-800 showed good humidity-sensitivity; the resistance values are fairly low at 33% rh (rh: relative humidity), and it changed by three orders of magnitude with increase in relative humidity in the range 33 to 94% rh. On the other hand, TiP-1-1000 scarcely exhibited humidity-sensitivity. Its resistance dependence on relative humidity resembles that for TiP-2-800.

Figure 4 shows the XRD patterns of TiP-1 heated at various temperatures. The XRD pattern of TiP-1 heated at 1000 °C was assigned to titanium pyrophosphate. TiP-1 heated at 400 to 800 °C will be a mixture of X-ray amorphous phase and titanium pyrophosphate. Comparison between Fig. 3 and Fig. 4 leads the conclusion that titanium pyrophosphate is not responsible for the humidity-sensitivity. It was also found that TiP-1-1000 was almost similar to that of TiP-2-800.

The very poor humidity-sensitivity of TiP-1-1000 may be related with the fact that the surface of TiP-1 heated at 1000 °C

FIGURE 3 Humidity-sensitive characteristics of TiP-1 as a function of sintering temperature.

FIGURE 4 Change in XRD pattern of TiP-1 heated at various temperatures

does not show any acidic property. This is because most POH groups of as-prepared TiP-1, which are known to provide protons, convert to POP groups on heating at a high temperature. In view of the above facts, a critical factor for excellent humidity-sensitivity of the TiP-1 is considered to be acidic POH groups on the surface of the amorphous phase (probably layered pyrophosphate), in addition to its suitable pore structure.

Figure 5 shows the effect of the sodium cation exchange on the humidity-sensitive characteristics of TiP-1. With increasing NaOH concentration, the resistance of the TiP-1-NaOH-800 disks decreased, especially in relative humidity range 0 to 33%. In order to examine the optimum stage of sodium cation exchange, 1.0 g of TiP-1 heated at 800 °C was dipped in a 0.1 M NaOH solution (200 ml) at room temperature for 15 h, and subsequently treated in the same way as described above. An element prepared from this material TiP-1-800-NaOH showed very poor humidity-sensitivity. Therefore, NaOH treatment should be made before calcining.

Figure 6 shows the change in XRD pattern of TiP-1 with NaOH treatment and of TiP-1-NaOH with heating. As-prepared TiP-1 (Fig. 6a) was transformed to amorphous phase after the treatment with

FIGURE 5 Humidity-sensitive characteristics of TiP-1-NaOH-800 prepared using different concentrations of NaOH solutions.

FIGURE 6 XRD pattern of TiP-1 (a), TiP-1-NaOH (b), and TiP-1-NaOH-800 (c).

NaOH solution. This will be caused by the destruction of the crystal structure of TiP-1. Figure 6c shows the XRD pattern of TiP-1-NaOH-800. This material is considered to be a mixture of amorphous phase and crystalline titanium pyrophosphate with weak diffraction intensity. This finding suggests that TiP-1-NaOH (Fig. 6b) was hardly be changed to crystalline titanium pyrophosphate (Fig. 6c). Probably PONA groups formed by NaOH treatment may prevent POH groups from undergoing condensation to POP groups. Consequently, the surface area will be kept fairly large, and Na^+ as well as H^+ will act as effective charge carriers.

Figure 7 shows the changes in resistance of TiP-1-800 and a commercial humidity sensor element and output voltage of the sensing device using them. The sensing device used was commercially obtained. Clearly the characteristics of the two elements were quite similar, indicating that TiP-1-800 element can replace the commercially used sensor element. It is noteworthy that when the resistance of each element is higher than ca. 20 M Ω , the output voltage becomes too low to be measured. Such a relationship was also

FIGURE 7 Resistance of TiP-1-800 and a commercial element and output voltage of the sensing device using them.

FIGURE 8 Output voltage of the sensing device using TiP-1-NaOH-800 and ZrP-NaOH-800.

observed for another TiP-1 elements tested. Therefore, it is necessary to lower the resistance of an element in relative humidity range 0 to 40%.

Figure 8 shows the change in output voltage of the sensing device using TiP-1-NaOH-800 and ZrP-NaOH-800 (ZrP: $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$) elements. The output voltage values in low relative humidity range were greatly improved. In addition, TiP-1-NaOH-800 element was superior to ZrP-NaOH-800 element in terms of linearity between output voltage and relative humidity.

In conclusion, TiP-1-NaOH-800 will be a promising candidate for humidity-sensitive materials.

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