

# Phosphorus solid solution effects of electric and dielectric properties on sintered $\text{WO}_3$ ceramics

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Phosphorus solid-soluted  $\text{WO}_3$  ceramics ( $\text{P}_x\text{W}_{1-x}\text{O}_3$ ) were fabricated by a solid state reaction at 1000°C for 100 h with the phosphorus concentration  $x$  of 0 to 0.3. Phosphorus-doped single-phase monoclinic  $\text{WO}_3$  ceramics were fabricated with phosphorus concentration between 0 and 0.3. Sintered  $\text{WO}_3$  pellets that were P-doped with phosphorus concentrations of 0–0.3 were synthesized at 1000°C in 24 h in order to evaluate electric and dielectric properties. The resistivity of specimens decreased concomitantly with increasing the stoichiometry  $x$  in  $\text{P}_x\text{W}_{1-x}\text{O}_3$  from 0 to 0.15, and that increased with increasing phosphorus concentration larger than 0.15. The dielectric constants of the specimens decreased with increase of phosphorus concentration, and the dielectric constant of the  $\text{P}_{0.05}\text{W}_{0.95}\text{O}_3$  and  $\text{P}_{0.10}\text{W}_{0.90}\text{O}_3$  were 2100 and 1400 at 100 kHz at room temperature, respectively.

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## 1. Introduction

Monoclinic tungsten trioxide ( $\text{WO}_3$ ) shows a high dielectric constant,<sup>1)–4)</sup> making  $\text{WO}_3$  ceramic a candidate for use in ceramic capacitors. However,  $\text{WO}_3$  resistivity is not high because oxygen defects exist in  $\text{WO}_3$ , producing electron carriers in  $\text{WO}_3$ .<sup>5),6)</sup> Consequently, it is difficult to use  $\text{WO}_3$  as a ceramic capacitor material.

A previous report describes a phosphorus-doped tungsten complex oxide ceramic ( $\text{ZrW}_2\text{O}_8\text{–Zr}_2\text{WP}_2\text{O}_{12}$ ),<sup>7)</sup> suggesting that phosphorus is substitutable for tungsten in a tungsten-based host structure. For  $\text{WO}_3$ , the valence of tungsten is six; if oxygen defects exist in  $\text{WO}_3$ , then the valences of tungsten are mixture of five and six, thereby; electron carriers are present in  $\text{WO}_3$  ceramics. The phosphorus valence in phosphates or complex oxides is five. For that reason, it is assumed that the valence of the phosphorus in a complex oxide  $\text{P–WO}_3$  is five. For this solid-solution  $\text{P–WO}_3$  oxide, a phosphorus solid soluted in  $\text{WO}_3$  might cause compensation of the electron carrier in  $\text{WO}_3$  generated by oxygen defects, which is expected to increase the resistivity of a  $\text{WO}_3$  host ceramic. That increased resistivity of  $\text{WO}_3$  host ceramic enables evaluation of the dielectric properties of  $\text{WO}_3$ .

In this investigation, phosphorus-doped  $\text{WO}_3$  ceramics were fabricated by a traditional solid state reaction, with the stoichiometry  $x$  in  $\text{P}_x\text{W}_{1-x}\text{O}_3$  between 0 and 0.3. Furthermore, the resistivity and dielectric property of the  $\text{P}_x\text{W}_{1-x}\text{O}_3$  ceramics were evaluated at room temperature.

## 2. Experimental procedure

The starting materials were  $\text{WO}_3$  (Wako Pure Chemical Industries, Ltd., Japan) and  $(\text{NH}_4)_2\text{HPO}_4$  (Wako Pure Chemical Industries, Ltd., Japan) powders. These powders were mixed with

the stoichiometry  $x$  in  $\text{P}_x\text{W}_{1-x}\text{O}_3$  between 0 (no mixed) to 0.3. Hereinafter,  $\text{P}_x\text{W}_{1-x}\text{O}_3$  means the  $x$  mol % solid solution of P in  $\text{WO}_3$ . The mixture was die-pressed to produce a pellet. The pellet was calcined at 1000°C for 2–100 h in air. It was then ground; the powder was die-pressed again using uniaxial pressing. The pellet was sintered at 1000°C for 24 h. Thereby; a phosphorus solid-soluted  $\text{WO}_3$  specimen was synthesized.

The crystal structure of the specimens was determined using X-ray diffraction (XRD, Miniflex-II; Rigaku Corp.) at room temperature with  $\text{Cu K}\alpha$ . The microstructural observation and the elementary analysis of the sample were done using scanning electron microscopy (SEM, S-3200N; Hitachi Ltd.) and energy dispersive X-ray analysis (EDX, EMAX-3000; Horiba Ltd.). The resistivity of the specimens was evaluated using a two-probe method with a digital voltmeter (34405A; Agilent Technologies Inc.) and a power supply (3640A; Agilent Technologies Inc.). Dielectric measurements were performed using an LCR meter (HP 4284A; Hewlett-Packard Inc.). All electrical measurements were conducted at room temperature.

## 3. Results and discussion

Ten % Phosphorus mixed  $\text{WO}_3$  ( $\text{P}_{0.1}\text{W}_{0.9}\text{O}_3$ ) samples were heat-treated at 1000°C for 2–100 h. **Figure 1** shows XRD patterns for the  $\text{P}_{0.1}\text{W}_{0.9}\text{O}_3$  ceramics under various heat-treatment times. For specimens heat-treated less than 35 h, a  $\text{WO}_3$  monoclinic structure (JCPDS 72-1465) was observed as a main phase, with a secondary phase [ $\text{W}_2\text{O}_3(\text{PO}_4)_2$ , JCPDS 76-1687]. However, for specimens heat-treated over 65 h, the XRD peaks of the specimens were assigned as a monoclinic  $\text{WO}_3$  single phase; no  $\text{W}_2\text{O}_3(\text{PO}_4)_2$  peak was observed.

**Figure 2** presents the SEM images and the elemental mapping images for phosphorus and tungsten of the  $\text{P}_{0.1}\text{W}_{0.9}\text{O}_3$  ceramic heat-treated at 1000°C for (a) 35 h and (b) 100 h. For the specimen that was heat-treated for 35 h, the elemental positions between phosphorus and tungsten almost fit each other. However,

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those of the grain boundary and at the grain surface were not fitted. Therefore, the reaction did not occur completely between  $\text{WO}_3$  and phosphorus at  $1000^\circ\text{C}$  for 35 h. For the specimen heat-treated for 100 h, the elemental positions of phosphorus and tungsten mutually coincided, and the reaction between phosphorus and  $\text{WO}_3$  proceeded completely at  $1000^\circ\text{C}$  for 100 h.

Results of XRD and the SEM-EDX measurements proved that the reaction time of phosphorus and  $\text{WO}_3$  must be longer than 65 h, and that the reaction occurred sufficiently more than the

heat-treatment time of 100 h. In this investigation, the specimens were heat-treated at  $1000^\circ\text{C}$  for 100 h.

The  $\text{P}_x\text{W}_{1-x}\text{O}_3$  ( $x = 0-0.3$ ) powders were reacted at  $1000^\circ\text{C}$  for 100 h. **Figure 3** shows XRD patterns for resulting specimens. All the samples with phosphorus contents  $x$  in  $\text{P}_x\text{W}_{1-x}\text{O}_3$  between 0 and 0.3 were assigned as a monoclinic  $\text{WO}_3$  single phase, and the another phases were not observed for all the

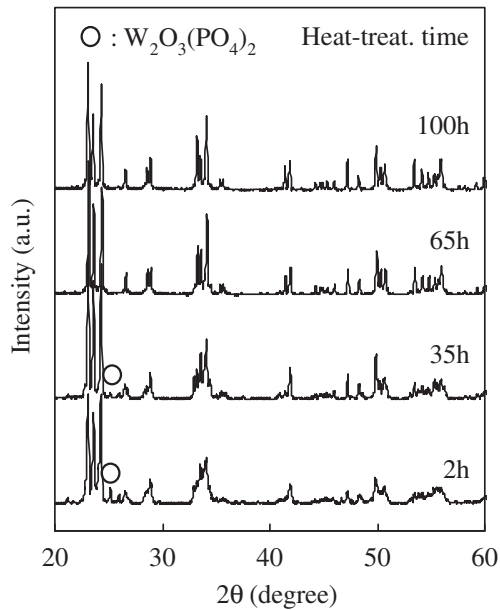


Fig. 1. XRD patterns for 10% phosphorus-doped  $\text{WO}_3$  specimens heat-treated at  $1000^\circ\text{C}$  for 2–100 h.

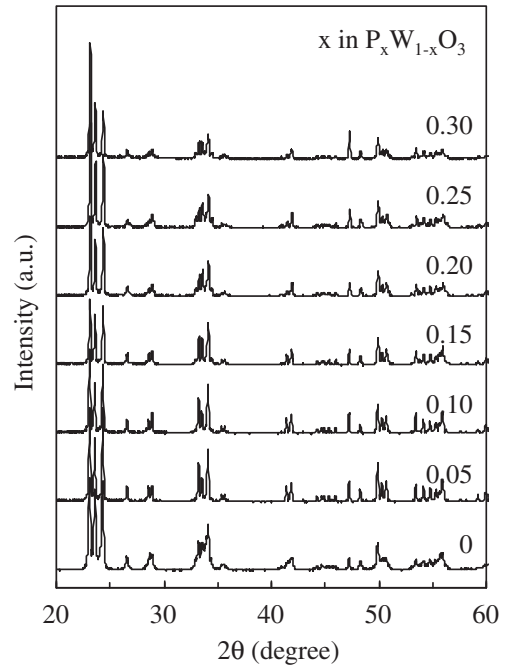


Fig. 3. XRD patterns for the  $x$  in  $\text{P}_x\text{W}_{1-x}\text{O}_3$  of 0–0.3 specimens heat-treated at  $1000^\circ\text{C}$  for 100 h.

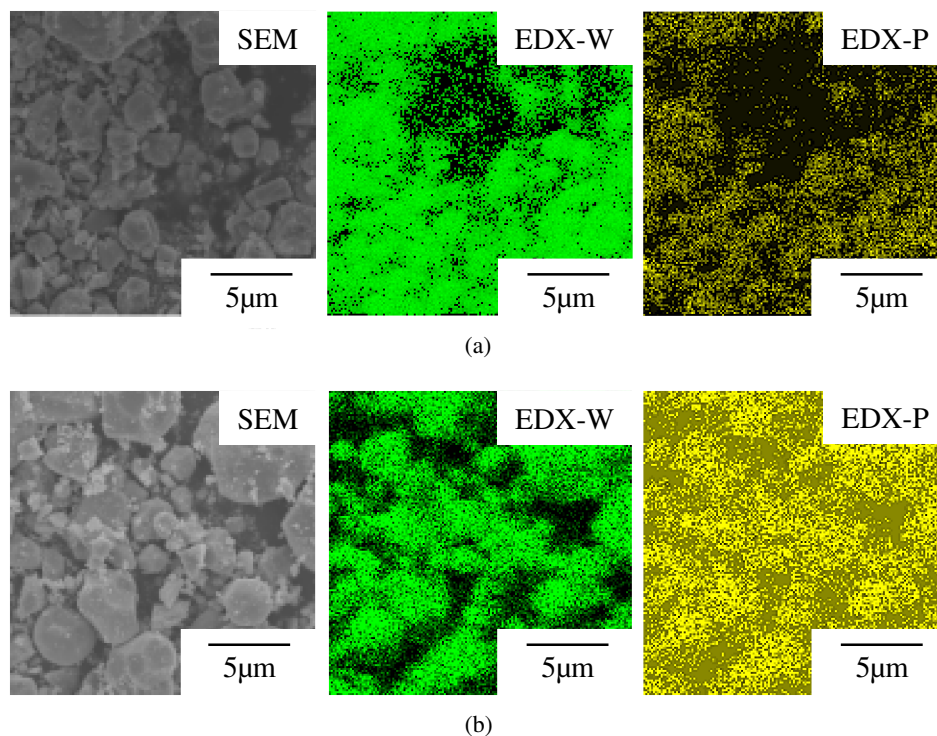


Fig. 2. (Color online) SEM-EDX images of the 10% phosphorus  $\text{WO}_3$  specimens heat-treated at  $1000^\circ\text{C}$  for (a) 35 and (b) 100 h.

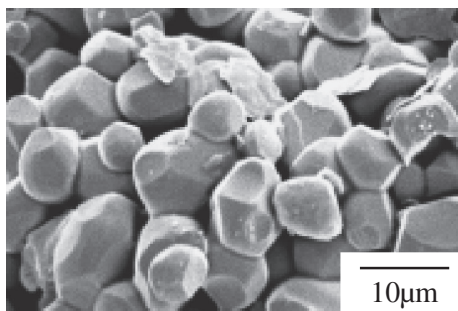


Fig. 4. An SEM image of the sintered  $\text{P}_{0.1}\text{W}_{0.9}\text{O}_3$  specimen heat-treated at  $1000^\circ\text{C}$  for 24 h.

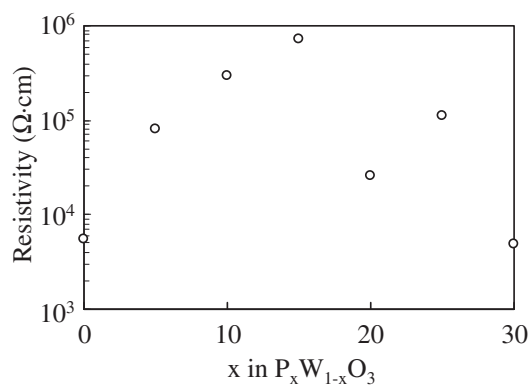


Fig. 5. Resistivity of the resulting  $\text{P}_x\text{W}_{1-x}\text{O}_3$  ( $x = 0-0.3$ ) specimens at room temperature.

specimens. These results suggest that the above heat-treatment condition was sufficient to be reacted phosphorus to  $\text{WO}_3$  host material.

Using these powders,  $\text{P}_x\text{W}_{1-x}\text{O}_3$  ( $x = 0-0.3$ ) pellets were fabricated at  $1000^\circ\text{C}$  for 24 h; the resulting ceramics with white-yellow color were used for measurements of electrical properties. **Figure 4** shows the SEM image of a sintered  $\text{P}_{0.10}\text{W}_{0.90}\text{O}_3$  pellet as a representative sample. From the SEM image, the resulting specimen was sufficiently sintered on the sintering condition, and the other samples were sintered under same sintering condition.

Resistivity of the resulting  $\text{P}_x\text{W}_{1-x}\text{O}_3$  sintered pellets was evaluated using a two-probe method. **Figure 5** portrays data showing the electrical resistivity of the specimens as a function of the phosphorus concentration in  $\text{WO}_3$ . Resistivity of the non-doped  $\text{WO}_3$  ceramic was  $5.4 \times 10^3 \Omega\cdot\text{cm}$ . That of  $\text{P}_x\text{W}_{1-x}\text{O}_3$  ceramics increased concomitantly with increased phosphorus concentration  $x$  of 0 to 0.15. The resistivity increased with increasing the phosphorus concentration  $x$  larger than 0.15, and the resistivity of the  $\text{P}_{0.3}\text{W}_{0.7}\text{O}_3$  was close to the non-doped  $\text{WO}_3$  ceramic. The resistivity of the resulting specimens with the  $\text{P}_{0.10}\text{W}_{0.90}\text{O}_3$ ,  $\text{P}_{0.15}\text{W}_{0.85}\text{O}_3$  was  $2.9 \times 10^5$ ,  $7.3 \times 10^5 \Omega\cdot\text{cm}$ , respectively. These values were 2 orders larger than that of the non-doped  $\text{WO}_3$  ceramic. Phosphorus, with a valence number of five, was doped into the  $\text{WO}_3$  host structure as the valence number of 6. Therefore, it assumed that the electron carrier as oxygen defect in  $\text{WO}_3$  was neutralized by a solid solution of phosphorus in a  $\text{WO}_3$  host.

**Figure 6** presents dielectric properties of the  $\text{WO}_3$  ceramics with phosphorus concentrations  $x$  of 0, 0.05, 0.10, and 0.15. Where, the dielectric constants of the other specimens were not evaluated because of their large dielectric losses. The dielectric loss of the non-doped  $\text{WO}_3$  specimen was very large between

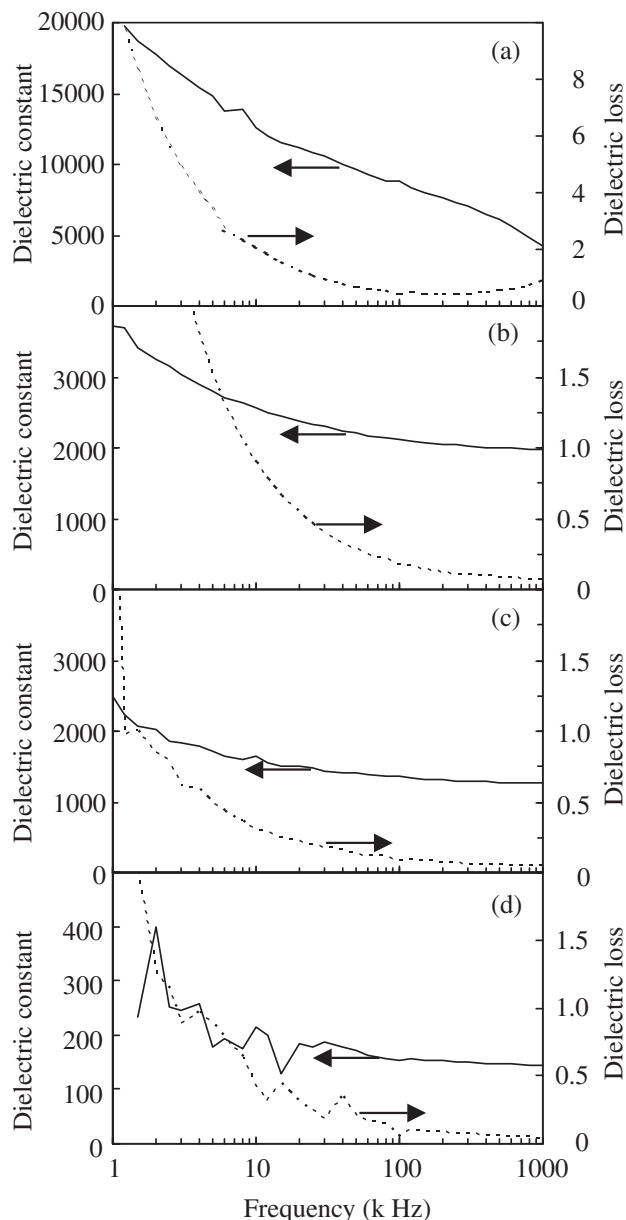


Fig. 6. Dielectric constant and loss of the  $\text{P}_x\text{W}_{1-x}\text{O}_3$  specimens: (a)  $x = 0$ , (b)  $x = 0.05$ , (c)  $x = 0.10$  and (d)  $x = 0.15$ .

1 kHz to 1 MHz, and the values were larger than 0.5. Therefore, it assumed that the dielectric constant of the non-doped  $\text{WO}_3$  could not be evaluated. At 1 kHz, the dielectric loss of these specimens was very large, close to 1, and the loss was less than 0.1 at frequencies higher than a few tens of kHz. The dielectric constants of the  $\text{P}_{0.05}\text{W}_{0.95}\text{O}_3$ ,  $\text{P}_{0.10}\text{W}_{0.90}\text{O}_3$ ,  $\text{P}_{0.15}\text{W}_{0.85}\text{O}_3$  were 2100, 1400 and 150 at 100 kHz. Increasing the phosphorus contents in the  $\text{WO}_3$  caused decreasing the dielectric constant of the specimens. Generally, dielectric constant depends on the electron density of the materials. The electron density of the phosphorus is much smaller than that of tungsten. In this article, phosphorus was substituted to the tungsten site in the  $\text{WO}_3$  host structure. Therefore, it assumed that increasing the phosphorus contents in the  $\text{WO}_3$  caused decreasing the dielectric constant of the specimens.

Hirose et al. reported that the dielectric constant of the non-doped  $\text{WO}_3$  ceramic was 4000 at  $16.2^\circ\text{C}$ ,<sup>4)</sup> and those of the

phosphorus-doped  $\text{WO}_3$  ceramic was smaller than the value reported for non-doped  $\text{WO}_3$  at 100 kHz. Therefore, it assumed that the doping phosphorus in  $\text{WO}_3$  host caused decreasing the dielectric constant of  $\text{WO}_3$ .

#### 4. Conclusion

Phosphorus-doped  $\text{WO}_3$  ceramic was fabricated at 1000°C for 100 h with phosphorus concentrations between 0 to 30%. Resistivity of the resulting specimens of  $\text{P}_{0.10}\text{W}_{0.90}\text{O}_3$ ,  $\text{P}_{0.15}\text{W}_{0.85}\text{O}_3$  was 2 orders larger than that of the non-doped  $\text{WO}_3$  ceramic. Oxygen defects acting as electron carriers in  $\text{WO}_3$  were neutralized by a solid solution of phosphorus in  $\text{WO}_3$ , proving that the electrical insulation of  $\text{WO}_3$  host ceramics is controllable by phosphorus doping of  $\text{WO}_3$ . The dielectric constants of  $\text{P}_x\text{W}_{1-x}\text{O}_3$  decreased with increase of the phosphorus contents in  $\text{WO}_3$  host ceramics.

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