Correlation between a dielectric anomaly and a phase transition of sintered phosphorus doped WO_3 ceramics

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Phosphorus doped WO_3 (P_xW_{1-x}O_3) ceramics were fabricated by a solid state reaction. Temperature and frequency dependence of dielectric properties for the P_xW_{1-x}O_3 (x=0–0.15) ceramics were evaluated at the temperature between -20 to 80°C. The dielectric constant of the P_{0.05}W_{0.95}O_3 ceramic was 3600–5800 at the frequency range from 1 kHz to 1 MHz in the room temperature, and the dielectric loss of the P_{0.05}W_{0.95}O_3 ceramic were less than 0.1 at the frequency of higher than 160 kHz. The dielectric anomaly peak of the WO_3 ceramic has been observed at about 0°C. The interaction between temperature dependence of dielectric properties (dielectric anomaly) ceramics and structural change of the WO_3 and P_{0.05}W_{0.95}O_3 were evaluated by Raman spectra.

Key-words : Tungsten trioxide, Dielectric property, Temperature dependence, Frequency dependence, Raman spectra

1. Introduction

Monoclinic tungsten trioxide (WO_3) shows a high dielectric constant, making WO_3 ceramic a candidate for use in ceramic capacitors. However, WO_3 resistivity is not high because oxygen defects exist in WO_3, producing electron carriers in WO_3 (1-4) (see Eq. (1), with Kröger Vink notation).

\[ O_3^* \rightarrow V_0^{**} + 2e^- + \frac{1}{2} O_2(gas) \]  

(1)

In previous report, we have fabricated phosphorus doped WO_3 ceramics, and have evaluated the dielectric property of the P_xW_{1-x}O_3 ceramics. When phosphorus with the valence of +5 was substituted to W in WO_3, it assumed that the electron carriers in WO_3 were canceled out as follows Eq. (2).

\[ \text{P(solid)} \xrightarrow{WO_3} \text{P}_{xW_{1-x}O_3} + h^* \]  

(2)

Though the dielectric property of phosphorus doped WO_3 (P_xW_{1-x}O_3) ceramic could be evaluated because of its high electrical resistivity, the temperature dependence of P_xW_{1-x}O_3 ceramic has not been measured. In this investigation, we observed the temperature dependence of the dielectric property of non-doped WO_3 ceramics and P_xW_{1-x}O_3 ceramics. Both of the specimens were observed dielectric anomaly, and thus, we evaluated the correlation between the temperature dependence of a dielectric property and the structure of the non-doped WO_3 ceramics.

2. Experimental procedure

The starting materials were WO_3 (Wako Pure Chemical Industries, Ltd., Japan) and (NH_4)_2HPO_4 (Wako Pure Chemical Industries, Ltd., Japan) powders. These powders were mixed with the stoichiometry x in P_xW_{1-x}O_3 between 0 to 0.15. The mixture was die-pressed to produce a pellet with 15 MPa. The pellet was calcined at 1000°C for 100 h in air. It was then ground and the PVA as binder was mixed; the powder was die-pressed again using uniaxial pressing with 15 MPa. The pellet was sintered at 1000°C for 24 h, thereby; a phosphorus solid-soluted WO_3 specimen was synthesized.

Crystal structure of the specimens was determined using X-ray diffraction (XRD, Miniflex; Rigaku Corp.) at room temperature with CuKα. Dielectric measurements were performed using an LCR meter (HP 4284A; Hewlett-Packard Inc.). Raman spectroscopy was carried out using a JASCO NR-1100 with a 532 nm line from an Nd:YAG laser.

3. Results and discussion

3.1 Dielectric property and temperature dependence

The P_xW_{1-x}O_3 (x=0–0.15) powders were reacted at 1000°C for 100 h. Figure 1 illustrates the XRD patterns for resulting specimens. All the samples with phosphorus contents x in P_xW_{1-x}O_3 between 0 and 0.15 were assigned as a monoclinic WO_3 single phase, and the other phases were not observed for all the specimens. These results were agreed well with the previous reports, and the resulting specimens could be used sufficiently for the electrical measurement.

Using these powders, the sintered P_xW_{1-x}O_3 (x=0–0.15) pellets for electrical measurements were fabricated at 1000°C for 24 h. Figure 2 presents dielectric properties of the WO_3 ceramics with phosphorus concentrations x of 0, 0.05, 0.10, and 0.15, and the measurement was carried out at room temperature of 20°C. The non-doped WO_3 indicated a huge-dielectric constant at the frequency between 1 kHz to 1 MHz, and the details were describes after. The dielectric loss of the non-doped WO_3 speci-
men was very large between 1 kHz to 1 MHz, and the values were larger than 0.5. The dielectric loss of the P_{0.05}W_{0.95}O_3 and P_{0.10}W_{0.90}O_3 was less than 0.1 at frequencies higher than 100 kHz. The dielectric constants of the P_{0.05}W_{0.95}O_3 was 3600–5800 at 100–1000 kHz. Increasing the phosphorus contents in the WO_3 caused decreasing the dielectric constant and increasing the dielectric loss of the specimens. To measure the dielectric property, a small dielectric loss value causes precisely measuring a dielectric constant. Thereby, we focused and investigated the P_{0.05}W_{0.95}O_3 ceramic to evaluate a temperature dependence of the dielectric property.

Temperature dependence of dielectric properties for the WO_3 and the P_{0.05}W_{0.95}O_3 ceramic was measured at the temperature range between −20 to 80°C, and the profiles were shown in Figs. 3 and 4. The non-doped WO_3 ceramic indicated a dielectric anomaly at the temperature of around 20°C, and the P_{0.05}W_{0.95}O_3 ceramic showed a dielectric anomaly at the temperature of around 0°C. The reason of the non-doped WO_3 having the huge dielectric constant at room temperature (see Fig. 1) was because the measurement temperature (20°C) of the sample was close to the anomaly temperature of the non-doped WO_3. The dielectric anomaly of the non-doped WO_3 ceramic was attributed to the phase transition from the monoclinic δ phase to the triclinic

![Image](https://example.com/image1.png)

Fig. 1. XRD patterns for the x in P_xW_{1-x}O_3 of 0–0.15 precursor powders.

![Image](https://example.com/image2.png)

Fig. 2. Dielectric constant and loss of P_xW_{1-x}O_3 (0–0.15) ceramics at the frequency between 1 kHz to 1 MHz.

![Image](https://example.com/image3.png)

Fig. 3. Temperature dependence of the dielectric constant and the loss of the WO_3 ceramic.
Hirose et al. reported that WO3 ceramic showed the dielectric anomaly at 17°C because of the phase transition, and our result was agreed well with the report. It assumed that the dielectric anomaly of the P0.05W0.95O3 ceramic was also attributed to the phase transition of WO3 (phosphorus doped WO3), and we investigated the correlation of the dielectric anomaly and the structure by Raman spectroscopy on the next section. For both samples, increasing temperature caused increase of the dielectric constants and the dielectric loss higher or lower than the dielectric anomaly temperature.

3.2 Raman spectra

In order to confirm between the dielectric property and the phase transition, Raman spectroscopy measurement was carried out for the WO3 and the P0.05W0.95O3 powder between −30 to 80°C.

Figure 5 portrays the Raman spectra for the WO3 powder. The peaks were observed at 130 (A), 264 (B), 320 (C), 701 (D) and 791 (E) cm⁻¹ for all the temperatures. These peaks were attributed to the WO3 monoclinic phase (γ) or the triclinic phase (δ). The peak A was associated to O–O deformation, the peaks B and C were assigned to W–O deformations, the peaks D and E were attributed to W–O stretching modes. All the peaks were sharpened and shifted to the position at the higher wavenumber position between 20–30°C, in particular, the peaks B and E changed remarkably. Figure 6 represents the positions and

Fig. 4. Temperature dependence of the dielectric constant and the loss of the P0.05W0.95O3 ceramic.

Fig. 5. Raman spectra of WO3 powder in the temperature range from −30 to 80°C with 10°C intervals.

Fig. 6. Temperature dependence of (a) the peak positions and the (b) integrated intensities of Raman peaks B and E.

Fig. 7. Raman spectra of P0.05W0.95O3 powder in the temperature range from −30 to 80°C with 10°C intervals.

Fig. 7. Raman spectra of P0.05W0.95O3 powder in the temperature range from −30 to 80°C with 10°C intervals.
the integrated intensity of the peaks B and E as a function of temperature. Beyond the temperature of 20–30°C, both of the peak positions shifted to high wavenumber, and the integrated intensities enhanced drastically. These change assumed to be the crystallographic transition of the WO₃, and the phase transition temperature agreed well with the dielectric anomaly temperature.

Figure 7 displays the Raman spectra for the P₀.₀₅W₀.₉₅O₃ powder. The peaks were observed at 132 (A’), 265 (B’), 323 (C’), 705 (D’) and 794 (E’) cm⁻¹ as well as the result of the non-doped WO₃, and these peaks were speculated to be the γ phase or the δ phase.⁹⁰ All the peaks were sharpened and shifted to the position at the lower wavenumber position between −20–0°C, in particular, a remarkable change was observed for the peaks B’ and E’. Figure 8 represents the positions and the integrated intensity of the peaks B’ and E’ as a function of temperature. Both of the peak positions shifted to low wavenumber at the temperature of −20 to −10°C, and the integrated intensities increased drastically at the temperature of −10–0°C. These results suggested that the phase transition of P₀.₀₅W₀.₉₅O₃ occurred at the temperature between −20–0°C. It assumed that the structural phase transition started at −20—10°C and occurred remarkably at −10–0°C. The results were agreed with the dielectric anomaly of the P₀.₀₅W₀.₉₅O₃ ceramic. Furthermore, the results of Raman spectra and dielectric anomaly suggested that phosphorus doping in WO₃ host causes decrease of the dielectric anomaly temperature.

4. Conclusion

Dielectric property and Raman spectroscopy observation was carried out for the PₓW₁₋ₓO₃ (x = 0–0.15) ceramics at various temperatures. The WO₃ ceramic and the P₀.₀₅W₀.₉₅O₃ ceramic indicated a dielectric anomaly at 17 and 0°C, respectively. By Raman spectra observation, the structural phase transition of the WO₃ ceramic and the P₀.₀₅W₀.₉₅O₃ ceramic were at the temperature of 20–30°C and −20–0°C, respectively. Thus, WO₃ dielectric anomaly temperature associating to phase transition decreased with increasing phosphorus contents in PₓW₁₋ₓO₃.

References