

Correlation between a dielectric anomaly and a phase transition of sintered phosphorus doped WO₃ ceramics

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Phosphorus doped WO₃ (P_xW_{1–x}O₃) ceramics were fabricated by a solid state reaction. Temperature and frequency dependence of dielectric properties for the P_xW_{1–x}O₃ (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}O₃ 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}O₃ ceramic were less than 0.1 at the frequency of higher than 160 kHz. The dielectric anomaly peak of the WO₃ ceramic has been observed at 20°C, and the dielectric anomaly peak of the P_{0.05}W_{0.95}O₃ ceramic has been observed at about 0°C. The interaction between temperature dependence of dielectric properties (dielectric anomaly) ceramics and structural change of the WO₃ and P_{0.05}W_{0.95}O₃ were evaluated by Raman spectra.

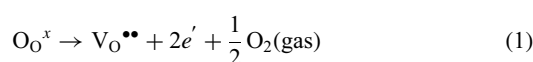
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1. Introduction

Monoclinic tungsten trioxide (WO₃) shows a high dielectric constant,^{1)–4)} making WO₃ ceramic a candidate for use in ceramic capacitors. However, WO₃ resistivity is not high because oxygen defects exist in WO₃, producing electron carriers in WO₃^{5),6)} (see Eq. (1), with Kröger Vink notation).



In previous report, we have fabricated phosphorus doped WO₃ ceramics, and have evaluated the dielectric property of the P_xW_{1–x}O₃ ceramics.⁷⁾ When phosphorus with the valence of “+5” was substituted to W (the valence of “+6”) site in WO₃, it assumed that the electron carriers in WO₃ were canceled out as follows Eq. (2).



Though the dielectric property of phosphorus doped WO₃ (P_xW_{1–x}O₃) ceramic could be evaluated because of its high electrical resistivity, the temperature dependence of P_xW_{1–x}O₃ ceramic has not been measured. In this investigation, we observed the temperature dependence of the dielectric property of non-doped WO₃ ceramics and P_xW_{1–x}O₃ 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 WO₃ ceramics and P_xW_{1–x}O₃ ceramics.

2. Experimental procedure

The starting materials were WO₃ (Wako Pure Chemical

Industries, Ltd., Japan) and (NH₄)₂HPO₄ (Wako Pure Chemical Industries, Ltd., Japan) powders. These powders were mixed with the stoichiometry x in P_xW_{1–x}O₃ 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 WO₃ specimen was synthesized.

The crystal structure of the specimens was determined using X-ray diffraction (XRD, Miniflex; Rigaku Corp.) at room temperature with Cu Kα. 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}O₃ (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}O₃ between 0 and 0.15 were assigned as a monoclinic WO₃ single phase, and the other phases were not observed for all the specimens. These results were agreed well with the previous reports,⁷⁾ and the resulting specimens could be used sufficiently for the electrical measurement.

Using these powders, the sintered P_xW_{1–x}O₃ (x = 0–0.15) pellets for electrical measurements were fabricated at 1000°C for 24 h. **Figure 2** presents dielectric properties of the WO₃ 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 WO₃ 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 WO₃ speci-

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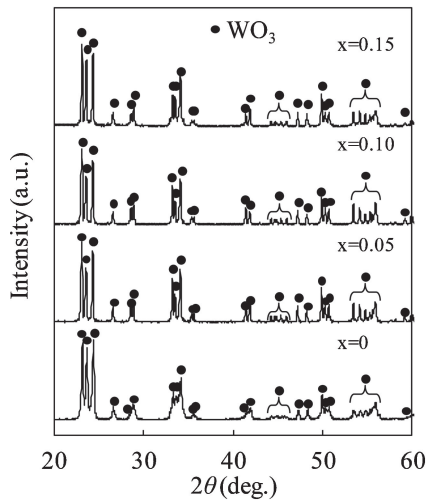


Fig. 1. XRD patterns for the x in $P_xW_{1-x}O_3$ of 0–0.15 precursor powders.

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 $80^\circ C$, 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 $20^\circ C$, and the $P_{0.05}W_{0.95}O_3$ ceramic showed a dielectric anomaly at the temperature of around $0^\circ C$. The reason of the non-doped WO_3 having the huge dielectric constant at room temperature (see Fig. 1) was because the measurement temperature ($20^\circ C$) 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

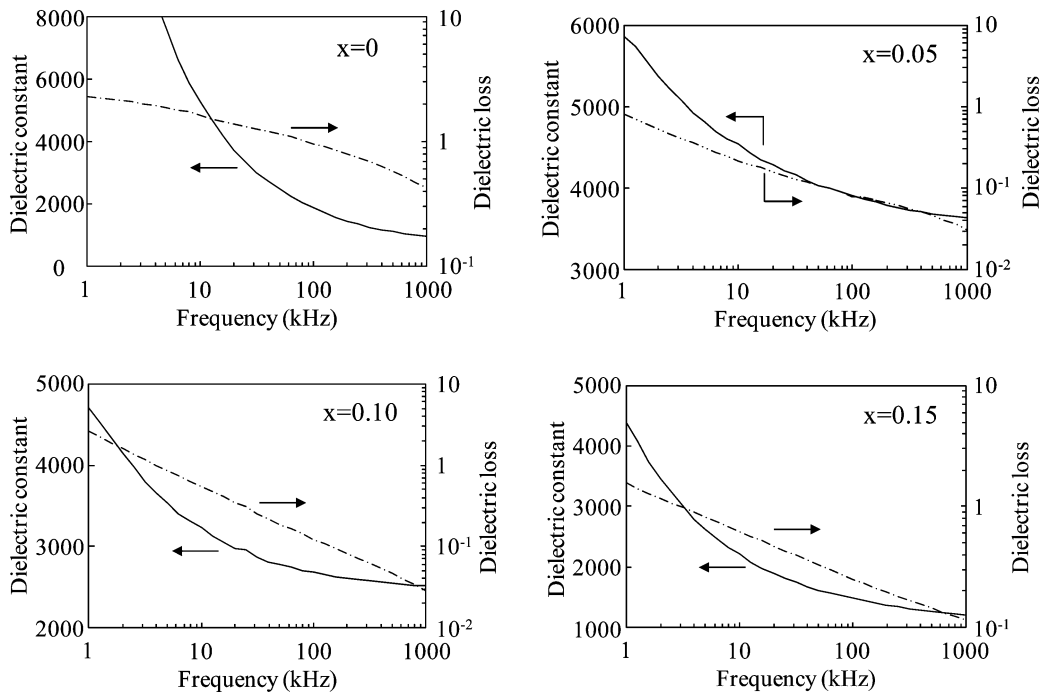


Fig. 2. Dielectric constant and loss of $P_xW_{1-x}O_3$ (0–0.15) ceramics at the frequency between 1 kHz to 1 MHz.

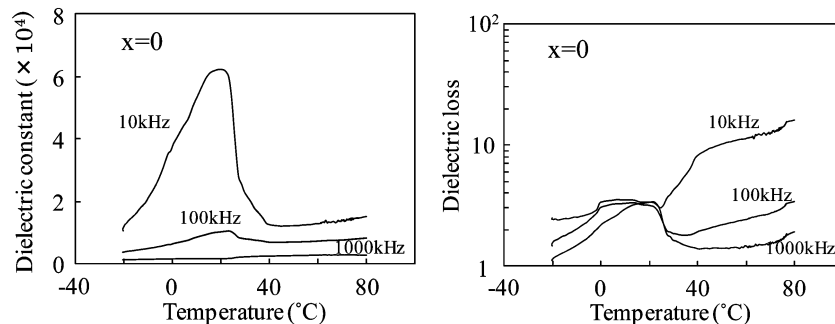


Fig. 3. Temperature dependence of the dielectric constant and the loss of the WO_3 ceramic.

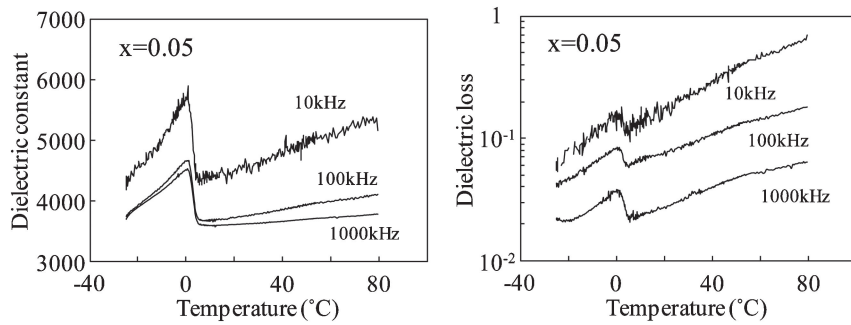


Fig. 4. Temperature dependence of the dielectric constant and the loss of the $P_{0.05}W_{0.95}O_3$ ceramic.

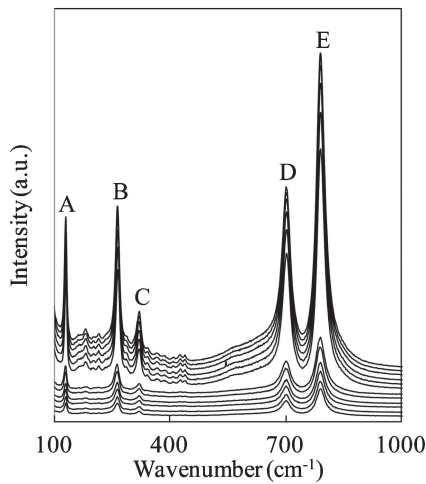


Fig. 5. Raman spectra of WO_3 powder in the temperature range from -30 to $80^\circ C$ with $10^\circ C$ intervals.

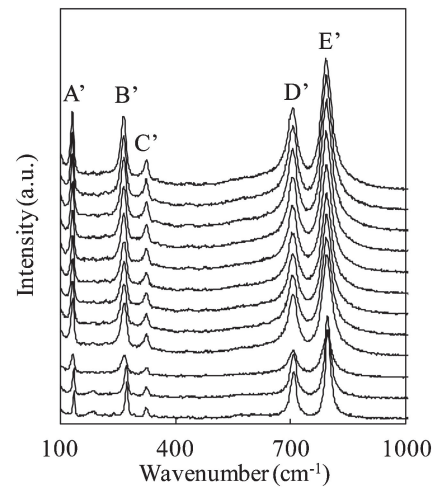


Fig. 7. Raman spectra of $P_{0.05}W_{0.95}O_3$ powder in the temperature range from -30 to $80^\circ C$ with $10^\circ C$ intervals.

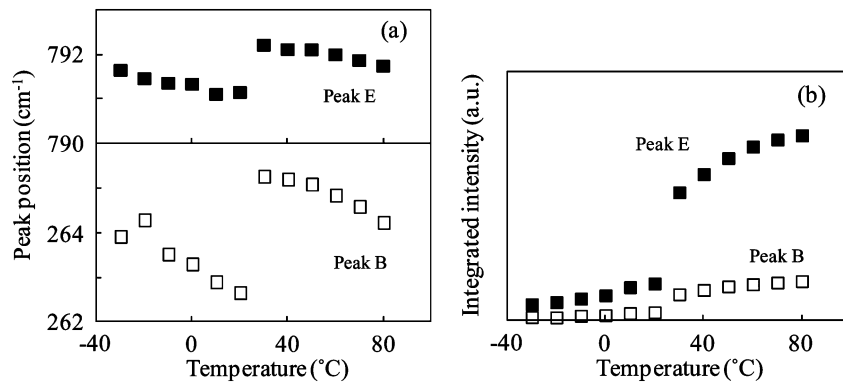


Fig. 6. Temperature dependence of (a) the peak positions and the (b) integrated intensities of Raman peaks B and E.

γ phase.⁸⁾ Hirose et. al reported that WO_3 ceramic showed the dielectric anomaly at $17^\circ C$ because of the phase transition, and our result was agreed well with the report.⁹⁾ It assumed that the dielectric anomaly of the $P_{0.05}W_{0.95}O_3$ ceramic was also attributed to the phase transition of WO_3 (phosphorus doped WO_3), and we investigated the correlation of the dielectric anomaly and the structure by Raman spectroscopy on the next section. For both of 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 WO_3 and the $P_{0.05}W_{0.95}O_3$ powder between -30 to $80^\circ C$.

Figure 5 portrays the Raman spectra for the WO_3 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 WO_3 monoclinic phase (γ) or the triclinic phase (δ).¹⁰⁾ The peak A was associated to O–O deformation,¹¹⁾ the peaks B and C were assigned to W–O deformations,¹²⁾ the peaks D and E were attributed to W–O stretching modes.¹²⁾ All the peaks were sharpened and shifted to the position at the higher wavenumber position between 20– $30^\circ C$, in particular, the peaks B and E changed remarkably. **Figure 6** represents the positions and

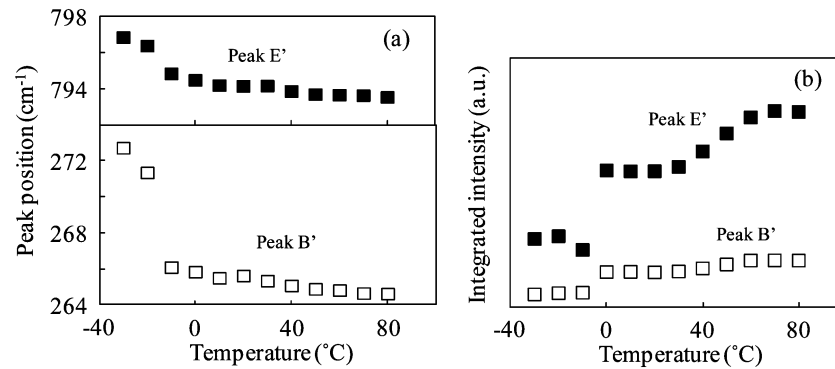


Fig. 8. Temperature dependence of (a) the peak positions and the (b) integrated intensities of Raman peaks B' and E'.

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 P_{0.05}W_{0.95}O₃ 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.¹⁰ 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–-10°C, and the integrated intensities increased drastically at the temperature of -10–0°C. These results suggested that the phase transition of P_{0.05}W_{0.95}O₃ 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 P_{0.05}W_{0.95}O₃ 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 P_xW_{1-x}O₃ ($x = 0-0.15$) ceramics at various

temperatures. The WO₃ ceramic and the P_{0.05}W_{0.95}O₃ 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 P_{0.05}W_{0.95}O₃ 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 P_xW_{1-x}O₃.

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