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Dielectric Properties of Selected Tungsten Compounds from 60 MHz to 9.44 GHz

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Crystalline powders of tungsten compounds ammonium paratungstate, ammonium metatungstate, tungsten trioxide hydrate ($WO_3 \cdot H_2O$), and tungsten blue oxide have been studied. The complex permittivity of the pulverized materials has been measured at room temperature from 60 MHz to 9.44 GHz. Intrinsic permittivity values of the crystalline solids have been derived from the apparent dielectric data of the powder material. Heating rate plots of powder samples of about 30 g at 2.45 GHz and 850 W radiation have also been taken. The slopes of the heating rate plots and the estimated dielectric loss factors of the crystalline solids are correlated. The experimentally observed microwave heating behavior and decomposition properties under microwave irradiation have been explained. © 1994 Academic Press, Inc.

INTRODUCTION

Dielectric properties of solids are investigated generally as part of the study of molecular behavior (1, 2). The preparation and characterization of special materials with high dielectric constant and low loss have been promoted by the increasing demands of the electronics industry. In the application of microwave energy for heating, firing, and calcination processes the knowledge of the dielectric properties at microwave frequencies is required to predict heating behavior (3). Data on the relative complex permittivity at microwave frequencies for most of the tungsten compounds cannot be found in the literature. Grain size and distribution (4–6) as well as thin shell inclusions on the grain surfaces (7, 8) are expected to have an influence on the dielectric properties of a granulated system. For the predicting of heating behavior it is also necessary to consider the effects of chemical impurities (9).

The electric properties of oxygen-deficient tungsten compounds WO_3, $W_xMo_{1-x}O_3$ (10, 11), and the M_xWO_3-type tungsten bronzes (12, 13) have received much attention over the past few decades. Their dielectric data cover a wide range depending on the structure and on the preparation conditions (14).

Tungsten compounds ammonium paratungstate (APT), ammonium metatungstate (AMT), and tungsten trioxide hydrate ($WO_3 \cdot H_2O$) selected in this study for determination of the dielectric properties are major basic materials of the tungsten industry (15). Tungsten blue oxide (TBO), a mixture of WO_3, $W_{20}O_{58}$, $W_{18}O_{49}$, ammonium, and hydrogen bronze phases, is obtained at the first reduction step in processing APT into tungsten powder (16, 17).

The purpose of this paper is to determine the macroscopic (apparent) or effective dielectric constant and dielectric loss of APT, AMT, $WO_3 \cdot H_2O$, and TBO powders in the high-frequency range, and to compare these data with microwave heating properties controlled by dielectric losses (8) and with the results of the observed microwave decomposition of APT (18).

EXPERIMENTAL DETAILS

Samples and Preparation

Dielectric and microwave heating measurements were performed on granular polycrystalline materials. APT

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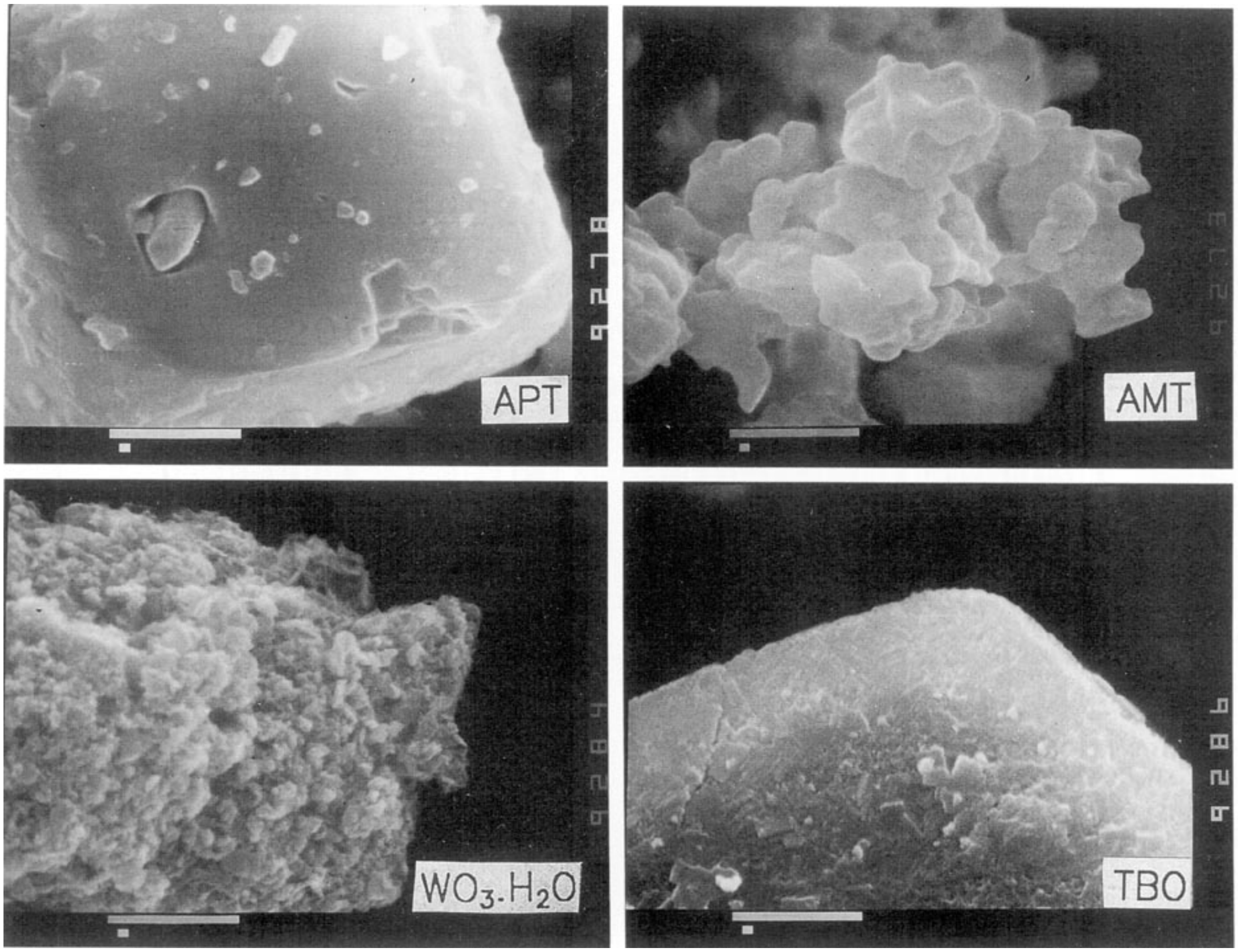

FIG. 1. Scanning electron micrographs of APT, AMT, $WO_3 \cdot H_2O$, and TBO used for dielectric measurements.

was obtained from Wolfram Bergbau und Hüttengesellschaft m.b.H., Bergla, Austria. AMT was prepared in our laboratory from ammonium tungstate solution by electrodialysis (19), and the resulting crystallites were then milled in a mortar. TBO was also prepared (from APT at 420°C in $N_2 + H_2$ mixture) and doped (K, Al, Si) in our laboratory. $WO_3 \cdot H_2O$ was purchased from China National Nonferrous Metals Import & Export Corporation. Scanning electron microscopy, X-ray diffraction, chemical analysis, and particle size analysis were performed for characterization of the samples for dielectric measurements. Scanning electron micrographs of the specimens and particle sizes and distributions are shown in Figs. 1 and 2. Table 1 summarizes the results of chemical analysis. Diffraction data on APT and $WO_3 \cdot H_2O$ were compared and checked with Joint Committee on Powder Diffraction Standards 1986 powder patterns, JCPDS 18127 and JCPDS 1418. Diffraction data taken on AMT were compared with the lines reported in Ref. (20), and the presence of AMT 2-6 and, to a lesser extent, AMT 12-15 is supposed. However, some lines in the diffraction pattern of AMT remained unidentified. Bulk densities of the samples (Table 2) were determined by dividing the weight of the samples by the volume they occupied in the sample holders.

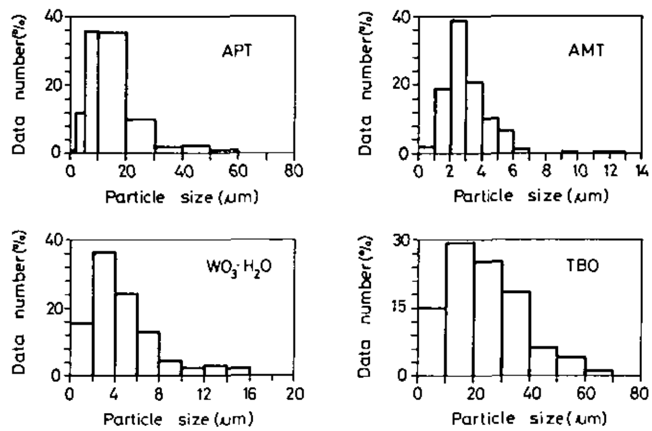

FIG. 2. Particle sizes and distributions for APT, AMT, $WO_3 \cdot H_2O$, and TBO powders used for dielectric measurements.

TABLE 1
Chemical Characteristics of Tungsten Compound Samples

Sample	WO_3 (%)	NH_3 (%)	Nonvolatile residue (%)	Impurity content (ppm)					
				Fe	Mo	Na	K	Si	Al
APT	89.1	5.3	0.01	3	15	1	1	10	10
AMT	91.6	3.0	0.05	28	108	344	3	10	10
$WO_3 \cdot nH_2O$	90.8	0	0.06	46	73	11	1	10	10
TBO	99.3	0.44	1.00	5	10	39	2340	2050	70

Note. Methods: WO_3%, ignition at 700°C/30 min; NH_3%, Kjeldahl method. Nonvolatile residue was gained in a stream of dry air saturated by CCl_4 at 550–570°C; the concentrations of Fe, Mo, Na, K, Si, Al are determined by atomic absorption spectroscopy, Na, K, Si, Al from the nonvolatile residue.

Dielectric Measurements

Three different measurement methods have been used:

(I) In the frequency range from 0.06 to 1 GHz the coaxial line method was used (21). A coaxial line was terminated by the test port (diameter = 20 mm, 5 mm long filled with the powder under test) and the reflection coefficient was measured by a computer-controlled impedance analyzer (Hewlett–Packard 4191A RF).

(II) From 1 to 9 GHz the measurements were made by the cavity perturbation method in the frequency domain with transmission technique. Two sizes of cylindrical cavity were used (diameter = 35 × 25 mm and 15 × 8 mm). The frequency was swept by a sweep oscillator (Hewlett–Packard 8350), and the signal was detected with a coaxial crystal detector. To evaluate the permittivity, two measurements were necessary for each sample on powder-filled and unfilled cavities. The two cavity sizes gave two resonant frequencies for each sample, at which the parameters were calculated. The sample holders were filled by gentle shaking and the filled sample holders were dried at 80°C for 1 hr. The complex permittivity has been measured at room temperature. Total time required for measurements according to methods I and II was about 2 hr.

(III) The cavity perturbation method (22) using small cylindrical sample holders (diameter = 2 × 20 mm, glass) was utilized for dielectric characterization at 9.44 GHz. A transmission type of rectangular cavity resonator gave the required sensitivity and accuracy.

TABLE 2
Powder and Bulk Densities of the Tungsten Compound Samples

	Powder density (g/ml)			
	APT	AMT	$WO_3 \cdot H_2O$	TBO
"Big" sample holder	2.72	2.43	1.0	2.6
"Small" sample holder	2.93	2.55	1.12	2.89
Bulk crystal	4.40	4.58	4.09	7.15

Note. "Big" sample holder used for measurements from 60 MHz to 9 GHz; "small" sample holder used for measurements at 9.44 GHz.

At the 9.44 GHz measurements the filled sample holders were attached first into the measuring cavity without drying and measured immediately. After the initial measurement was taken, the sample holder was removed from the system and put into the drying oven. After drying at 80°C for 1 hr the sample holder was again attached to the system and another measurement was taken.

The influence of the storage time under exposure of the atmosphere on the permittivity of the originally dried APT powder was also investigated at 9.44 GHz. In this experiment oven-dried samples (10 pieces) were attached to the measuring system. After 30 sec the temperature of the samples, as it was registered in a supplemental experiment, reached room temperature, and after another 10 sec the first measurements were taken. The samples were allowed to be exposed to the atmosphere in their individual sample holders and permittivity measurements were repeated on each sample after 1 hr, 1 day, and 1 week. Dehydration and water uptake were monitored by measuring the weight changes.

Microwave Heating Experiments

Microwave heating of APT, AMT, $WO_3 \cdot H_2O$, and TBO (23) was carried out in a 2.45-GHz commercial oven at 85, 255, and 850 W nominal values of power. A 1000-ml water-containing Pyrex beaker was placed in the oven for protection of the power tube. Powder samples were placed into a silica test-tube (i.d. = 23 mm, powder height = 25 mm). Samples for the microwave heating experiments were used without preliminary drying, as received and stored in sealed bottles. The sample holder was placed into the oven, the microwave radiation was switched on for 1–3 min, and after this heating period a thermocouple with low heat capacity was inserted midway into the powder. The maximum temperature obtained in this way was taken to be the temperature of the sample

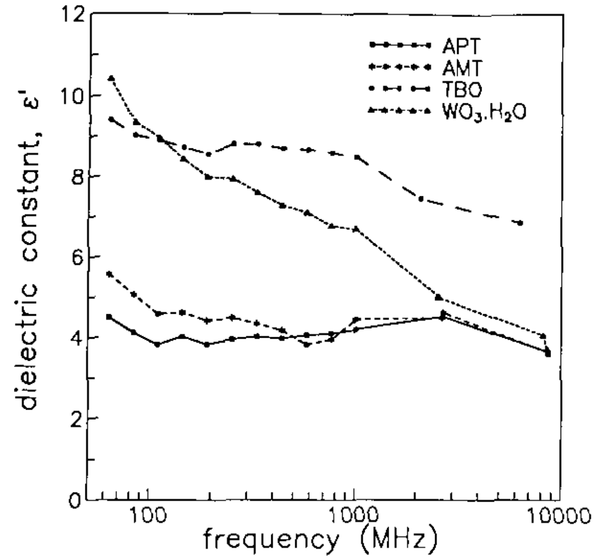

FIG. 3. Dielectric constant (real part, ε') of APT, AMT, $WO_3 \cdot H_2O$, and TBO vs frequency measured at room temperature after 80°C/1 hr air drying. Powder densities, $\rho_{APT} = 2.7 \pm 0.1$ g cm^{-3}, $\rho_{AMT} = 2.43 \pm 0.04$ g cm^{-3}, $\rho_{WO_3 \cdot H_2O} = 1.0 \pm 0.1$ g cm^{-3}, and $\rho_{TBO} = 2.6 \pm 0.1$ g cm^{-3}.

after a heating period. The sample holder without the thermocouple was then put back and the microwave oven switched on again. The water in the Pyrex beaker was changed after every heating period. Secondary, nonmicrowave heating effects were taken into account by registering the temperature rise of high purity, low dielectric loss Al_2O_3 powder placed in the same sample holder in a similar way.

EXPERIMENTAL RESULTS

TABLE 3

Permittivity Values of Powder-like Tungsten Compounds Measured at 9.44 GHz

		Dielectric constant, ε'	Dielectric loss factor, ε"
APT	As received	4.39 ± 0.27	0.19 ± 0.01
APT	Dried	3.92 ± 0.09	0.062 ± 0.008
AMT	As received	4.84 ± 0.08	0.17 ± 0.009
AMT	Dried	4.77 ± 0.04	0.148 ± 0.004
$WO_3 \cdot H_2O$	As received	5.00 ± 0.32	0.645 ± 0.11
$WO_3 \cdot H_2O$	Dried	4.61 ± 0.23	0.35 ± 0.05
TBO	As received	10.75 ± 0.81	0.44 ± 0.18
TBO	Dried	10.37 ± 0.84	0.27 ± 0.12

Dielectric constants of the dried samples measured from 60 MHz to 9 GHz are plotted in Fig. 3 versus the frequency. The values of the macroscopic dielectric constant of AMT and APT powders are close to each other and their behavior over the measured frequency range is similar. TBO has a higher macroscopic dielectric constant, with a similar frequency behavior. The dielectric constant of $WO_3 \cdot H_2O$ decreases during the investigated frequency range and approaches the value of APT and AMT at about 2 GHz. A slight decrease of the dielectric constant values of all of the four powders was observed between 3 and 9 GHz.

Table 3 summarizes the results of the measurements at 9.44 GHz. The influence of the storage time (in air, at 21°C and 70% RH) on the dielectric constant and dielectric loss factor of the originally dried APT and relative changes in weight of APT is shown in Figs. 4 and 5.

Microwave heating resulted in an increase of temperature of each sample at all power levels used. Temperature profiles in time at 85, 255, and 850 W microwave heating of the tungsten compound powders: APT, AMT, $WO_3 \cdot H_2O$, and TBO are shown in Fig. 6. The higher level of micro-

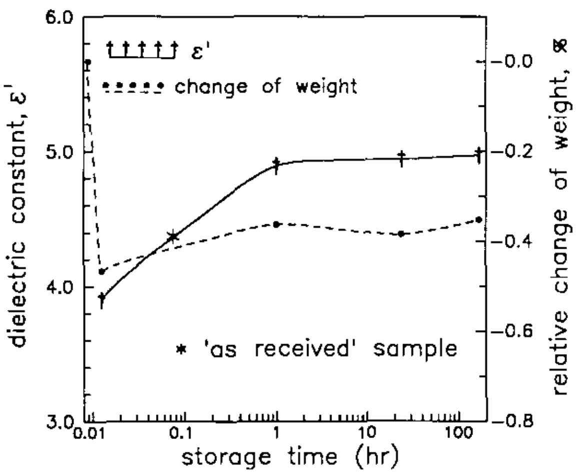

FIG. 4. Variation of weight and dielectric constant (real part, ε') of APT dried in air at 80°C, 1 hr, vs storage time (in air, at 21°C, 70% RH) measured at 9.44 GHz. The star (⋆) shows the dielectric constant measured on sample "as received."

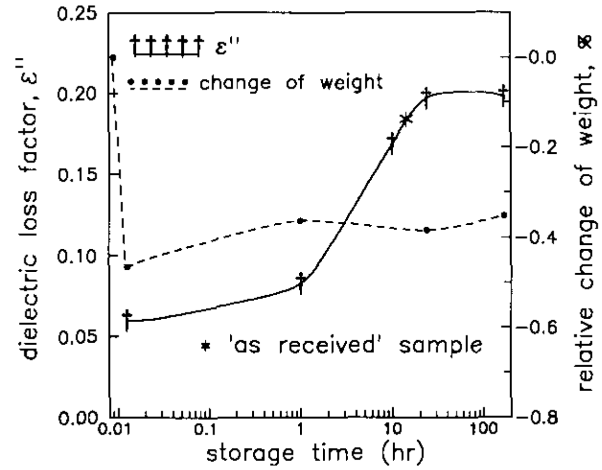

FIG. 5. Variation of weight and dielectric loss factor (imaginary part, ε") of APT dried in air at 80°C, 1 hr, vs storage time (in air, at 21°C, 70% RH) measured at 9.44 GHz. The star (⋆) shows the dielectric loss factor measured on sample "as received."

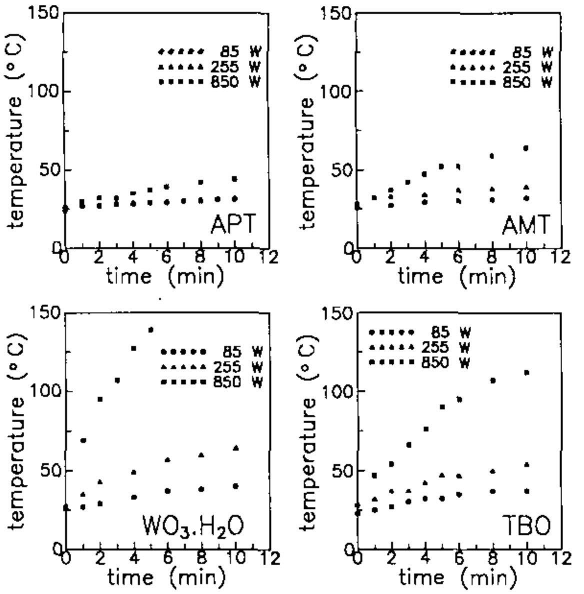

FIG. 6. Plots of temperature rise of pulverized tungsten compounds heated in a 2.45-GHz microwave oven at 85, 255, and 850 W nominal values of microwave power level. Powder height = 25 mm; diameter = 23 mm.

wave radiation results in a steeper slope of temperature rise. The slopes of the temperature versus time plots (*dT/dt*) at room temperature are shown in Table 4.

DISCUSSION

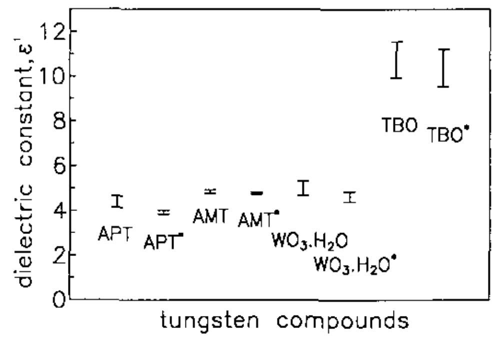

FIG. 7. Range of the standard deviation of dielectric constant (real part, ε') measured by cavity perturbation method at 9.44 GHz, room temperature. Samples of APT, AMT, $WO_3 \cdot H_2O$, and TBO from closed containers are measured just after charging the sample holders and again after drying at 80°C, 1 hr (*). Powder densities: $\rho_{APT} = 2.93$ g cm^{-3}, $\rho_{AMT} = 2.7$ g cm^{-3}, $\rho_{WO_3 \cdot H_2O} = 1.12$ g cm^{-3}, and $\rho_{TBO} = 2.89$ g cm^{-3}.

Experimental data on permittivity values at 9.44 GHz (Table 3) are demonstrated in Figs. 7 and 8. Ranges of scattering in measured values for "as-received" and dried samples are separately depicted. In the case of APT it is shown (Figs. 4 and 5) that "as-received" values are between the dried and the "as-saturated under air exposure" values. From the point of view of the dielectric constant, ε', the investigated materials fall into two classes (Fig. 7). APT, AMT, and $WO_3 \cdot H_2O$ represent a group of materials characterized by low dielectric constant, while TBO has a comparatively high dielectric constant. APT, AMT, and $WO_3 \cdot H_2O$ are stoichiometric compounds of the same oxidation state of tungsten, and electron polarizabilities of the molecule crystals of such compounds may be supposed to be similarly low at about 9 GHz. On the other hand, some components of the TBO phase mixture exhibit extremely high dielectric constant (11). From the point of view of the dielectric loss factor, ε", the low-loss APT and AMT can be separated from $WO_3 \cdot H_2O$ and TBO

TABLE 4

Slopes of the Temperature Rise Curves, (*dT/dt*), at Room Temperature, at 2.45 GHz Microwave Heating of Pulverized Tungsten Compound Samples

	Slope of temperature rise (°C/min)		
	85 W	255 W	850 W
APT	0.48	0.62	2.2
AMT	0.61	1.19	4.8
$WO_3 \cdot H_2O$	1.89	5.3	40
TBO	1.07	4.3	11.7
Al_2O_3	0.22	0.5	2.1

Note. Powder height = 25 mm; diameter = 23 mm. *dT/dt* values of Al_2O_3 powder (permittivity of the pressed polycrystal: ε' = 9.5; ε" < 10^{-3}) are shown for comparison and demonstration of the background temperature rise.

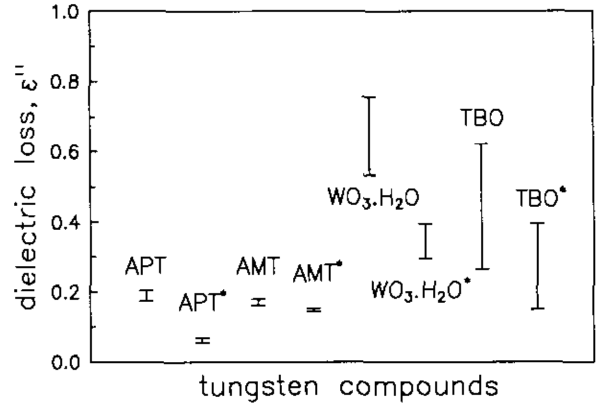

FIG. 8. Range of the standard deviation of dielectric loss factor (imaginary part, ε") measured by cavity perturbation method at 9.44 GHz, room temperature. Samples of APT, AMT, $WO_3 \cdot H_2O$, and TBO from closed containers are measured just after charging the sample holders and again after drying at 80°C, 1 hr. (*). Powder densities: $\rho_{APT} = 2.93$ g cm^{-3}, $\rho_{AMT} = 2.7$ g cm^{-3}, $\rho_{WO_3 \cdot H_2O} = 1.12$ g cm^{-3}, and $\rho_{TBO} = 2.89$ g cm^{-3}.

exhibiting higher dielectric loss (Fig. 8). It should be noted that dielectric loss data of TBO have a rather high scattering. This seems to be associated with the highest grain size (Fig. 2) and the mixed phases of the sample. $WO_3 \cdot H_2O$ is characterized by a marked difference in the dielectric loss factor of the "as-received" and "dried" state of the sample.

The dielectric properties of tungsten trioxide hydrates prepared by sol-gel processes and appropriate heat treatment have extensively been investigated by Gacoin *et al.* (24). From the data of the Cole–Cole plot of $WO_3 \cdot H_2O$ in (24) a similar nature of the relationship between dielectric constant and frequency can be seen as it is observed in the present study (Fig. 3). In (24) this behavior of the ε' versus frequency plot is attributed to the coordinated water (*y* water) "bonding" WO_3 layers in $WO_3 \cdot H_2O$ crystal. Such coordinated water cannot be found in the crystals built of paratungstate or metatungstate ions (25) or in the dehydrated tungsten oxide crystals. The differences in the behavior of ε' as a function of frequency found in our experiments (see Fig. 3) seem to be consistent with the presence or absence of the coordinated water (*y* water).

One main purpose of this study is to correlate the observed heating curves and the measured permittivity values of the investigated samples. Heating curves were taken at 2.45 GHz. Unfortunately we could not measure dielectric loss factors at this frequency. From the dielectric constant versus frequency plots (Fig. 3) it may be supposed that permittivity values do not change very rapidly in the frequency range from 2.45 to 9.44 GHz; therefore, the permittivity values measured at 9.44 GHz are considered in the following for comparison with the heating properties at 850 W. (At this level of microwave radiation background changes in temperature seem to be less disturbing.)

Permittivity data measured on pulverized samples with the consideration of the powder densities have been used for the estimation of the permittivity values of the bulk crystals. Two methods, the one suggested by Neelakantaswamy *et al.* (26) and the other suggested by Looyenga (27), have been used. The values estimated from the results measured in various sample holders (differing powder densities) and at possibly close frequencies are given in Table 5.

The dielectric constant of pressed pellets of $WO_3 \cdot H_2O$ has been measured in (24) as $\varepsilon_\infty \approx 20$. The dielectric constant of a bulk crystal may be somewhat higher, but it is evident that our estimated data given in Table 5 as 31 or 59 for the "big" sample holder are too high. Estimations from the results measured in the "small" sample holder yield even higher values. Although the application of the methods proposed in both (26) and (27) is evidently limited by the shortcomings of the measurement of the powder density, the shape of the crystallites, and the grain size and distribution, the permittivity data given in Table 5 seem to be useful in explaining the microwave heating properties of the investigated tungsten compounds. In Fig. 9 the dielectric loss factors estimated by the methods of both Neelakantaswamy *et al.* (26) and Looyenga (27) are plotted as a function of the slope of

TABLE 5

Permittivity Values of Compact Tungsten Compound Crystals Estimated by the Methods of Looyenga (27) and Neelakantaswamy *et al.* (26)

		f (GHz)	Θ	ε'	tanδ
APT "small" holder	(26)	9.14	0.666	7.7	0.023
	(27)	9.14	0.666	23.5	0.05
"big"	(26)	8.66	0.61	8.1	
	(27)	8.66	0.61	31.2	
AMT "small" holder	(26)	9.14	0.557	15.3	0.055
	(27)	9.14	0.557	53.6	0.097
"big"	(26)	8.63	0.53	11.3	
	(27)	8.63	0.53	54	
$WO_3 \cdot H_2O$ "small" holder	(26)	9.14	0.274	233	0.279
	(27)	9.14	0.274	599	0.436
"big"	(26)	8.5	0.32	59	
	(27)	8.5	0.32	31	
TBO "small" holder	(26)	9.14	0.40	358	0.061
	(27)	9.14	0.40	330	0.139
"big"	(26)	6.27	0.36	209	
	(27)	6.27	0.36	348	

Note. Loss tangent data for both sample holders were gained from the measurements made in the "small" sample holder. *f*, measuring frequency; Θ, fractional volume of the powder particles in the sample holder; ε', dielectric constant; tanδ (loss tangent) = $\varepsilon''/\varepsilon'$.

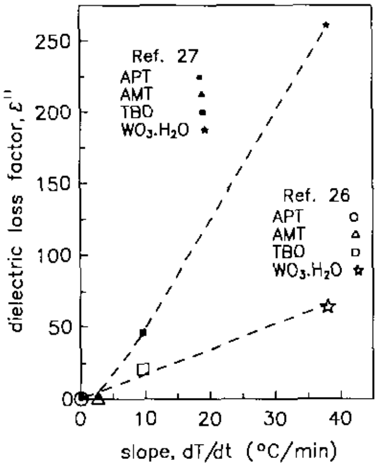

FIG. 9. Dielectric loss factors (imaginary part, ε'') of the crystalline solids (APT, AMT, TBO, and $WO_3 \cdot H_2O$) estimated by methods (26, 27) from apparent loss factor of the powders at 9.44 GHz vs corrected slope of the temperature rise curves, *dT/dt* at 850 W. Slopes for APT, AMT, TBO, and $WO_3 \cdot H_2O$ from Table 4 are corrected by observed slope of temperature rise in Al_2O_3.

the heating curves from the 850 W/2.45 GHz experiments. (Data from Table 4 were corrected by 2.1°C/min dT/dt value of Al_2O_3.) Dielectric loss factor values estimated by both methods seem to be close to the linear relationship described by the heating rate formulas of Tinga (8). This linear relationship between the dielectric loss factor and the observed heating rate properties seems to be convincing if we consider that experimental points are relating various kinds of chemical substances with somewhat differing density, specific heat, and internal electric field.

With the help of the measured permittivity values we suggest an interpretation on the microwave decomposition properties of APT and AMT (18). APT powder samples were reported not to change at 500 W/2.45 GHz microwave radiation, while AMT crystals collapsed. According to the permittivity values given in Table 5 the dielectric constant and $\tan\delta$ of AMT are twice as high (dielectric loss factor four times as high) as the parameters of APT. Dielectric heat generated in the APT crystallites is much less than that generated in AMT and causes only limited dehydration of APT. With the progress of drying the dielectric loss factor decreases, and at a relatively low temperature the generated heat and the lost heat will equilibrate. In the bulk of the AMT crystallites, however, the local temperature is high enough to release the water of crystallization. The released water trapped on the surface of the powder-like sample increases the effective dielectric loss factor. Whether the temperature stabilizes at a higher temperature or a thermal "run away" advances from localized sites in the reaction volume depends on size, dimension, and the possibilities of exhalation.

The decomposition of APT at 3000 W/2.45 GHz radiation reported in (18) can be interpreted in a similar way. The applied high electric field causes a temperature rise in the internal part of the pulverized sample, which is high enough for the release of the first water of crystallization, while the silica tube container hinders the exhalation of the moisture. Then the process will progress especially because some solid decomposition products of APT possess extremely high dielectric loss factors.

SUMMARY AND CONCLUSION

The complex permittivity of APT, AMT, $WO_3 \cdot H_2O$, and TBO powders has been measured from 60 MHz to 9.44 GHz. Permittivity changes of APT through the storage time at standard air ambient have been demonstrated. Heating rate plots at 2.45 GHz and 850 W radiation have been taken. The frequency-dependent measurement of the dielectric constant has lead to the selection of $WO_3 \cdot H_2O$ as a compound containing "bonding" coordinated water (y water) in the crystal lattice, consistent with (24).

The slopes of the heating rate plots and the dielectric loss factors of the crystalline solids estimated by two different methods (26, 27) were found to be close to a linear relationship predicted in (8). Permittivity data, dehydration curves, and findings on APT and AMT decomposition (18) suggest that a number of non-dielectric parameters, dimension of powder bed, gas permeability, dielectric properties of decomposition products influence the result of interaction between tungsten oxide compounds and microwaves.

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