

High Temperature W-band Complex Permittivity Measurements of Thermally Cycled Ceramic-Metal Composites: AlN:Mo with 0.25 vol% to 4.0 vol% Mo from 25 °C to 1000 °C in Air

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Abstract

An apparatus for measuring the W-band (75-110GHz) complex permittivity of dielectrics at 1000 °C was developed. This apparatus allows for measurements at approximately twice the temperature of previously published high temperature free-space measurement systems while maintaining similar precision. Challenges were addressed related to high temperature measurements, including temperature uniformity, the accuracy of temperature measurements, and preventing temperature related changes to mm-wave measurement systems. The details of complex permittivity extraction from the measured S-parameters are discussed. Sources of error related to permittivity measurement and mathematical models were identified and are discussed in detail herein. Thermally-cycled, mm-wave absorbing, aluminum nitride ceramic composites containing varying levels of molybdenum additives were measured over the range of 25-1000 °C. These measurements were compared to the same composites before thermal cycling. It was found that ceramic composites are largely stable after thermal cycling in terms of dielectric properties despite the presence of visible surface modifications.

1. Introduction

Aluminum nitride ceramics with metal powder additives, such as molybdenum, have been proposed for use as high temperature susceptor materials for millimeter wavelength radiation¹. One specific application proposed for these materials is for a millimeter wave radiation-powered heat exchanger for power beaming applications¹⁻³. The AlN:Mo material system, having a highly thermally conductive matrix (AlN)^{4,5} and tunable mm-wave absorption properties by way of Mo powder loading, is a promising material system for these types of applications.

Previous studies of the W-band (75 GHz – 110 GHz) dielectric properties of the present AlN:Mo system, having Mo concentrations ranging from 0.25 vol% to 4 vol%, were limited to temperatures below 550 °C¹; however, predicted operating parameters for an envisioned mm-wave heat exchanger experiment involve cycling to substantially higher temperatures (600-1000 °C) for multiple hours in air. To enable complex permittivity measurements to be performed at temperatures up to 1000°C, modifications to an existing high-temperature, free-space, permittivity characterization system⁶ were necessary to extend the original [550 °C] temperature limit.

A brief discussion of AlN:Mo sample preparation is provided in Section 2. The subsequent sections describe the modified high temperature free space measurement system (Section 3) and provide examples of data reduction (Section 4) and uncertainty analysis (Section 5). Section 6 provides results from dielectric property measurements of the thermally cycled AlN:Mo samples. These results are compared to previously published measurement data for the same samples, prior to thermal cycling¹. Finally, a closing summary is provided in Section 7.

2. Sample Preparation

The six AlN:Mo samples, having Mo concentrations of 0.25%, 0.5%, 1.0%, 2.0%, 3.0% and 4.0%, by volume, were the same originally analyzed at lower temperatures (25 to 550 °C) in Ref. 1. During fabrication, each sample was sintered by hot pressing at 1900 °C in an inert atmosphere, cooling to room temperature, then machining into a disk (0.635 cm thick, 5.08 cm diameter). In addition to the AlN and Mo phases comprising the samples, small amounts of additives formed during sintering were present, including Y₂O₃ (5.0 vol%) and carbon (0.5 vol%), which serve as sintering aids, as well as YAlO₃ (~6% vol%) and Mo₂C (~0.5 vol%) reaction byproducts.¹

In preparation for the present measurements, each of the AlN:Mo samples was thermally cycled from 25 °C to 1000 °C ten times in air. The samples were heated in a CM 1700 box furnace (Pacific Combustion Engineering Company, Torrance, CA, USA). Each furnace heating cycle consisted of a ramped heat-up at 2 °C/min followed by a 1-hour hold at 1000 °C. The samples were then allowed to cool down to room temperature over a six-hour period. The thermally cycled samples were observed to have developed a light-colored patina on portions of the outer surfaces, as shown in Figure 1 (b), that was not present prior to thermal cycling (Figure 1 (a)). A microstructural analysis of this patina is ongoing⁷ and will be presented elsewhere when complete.

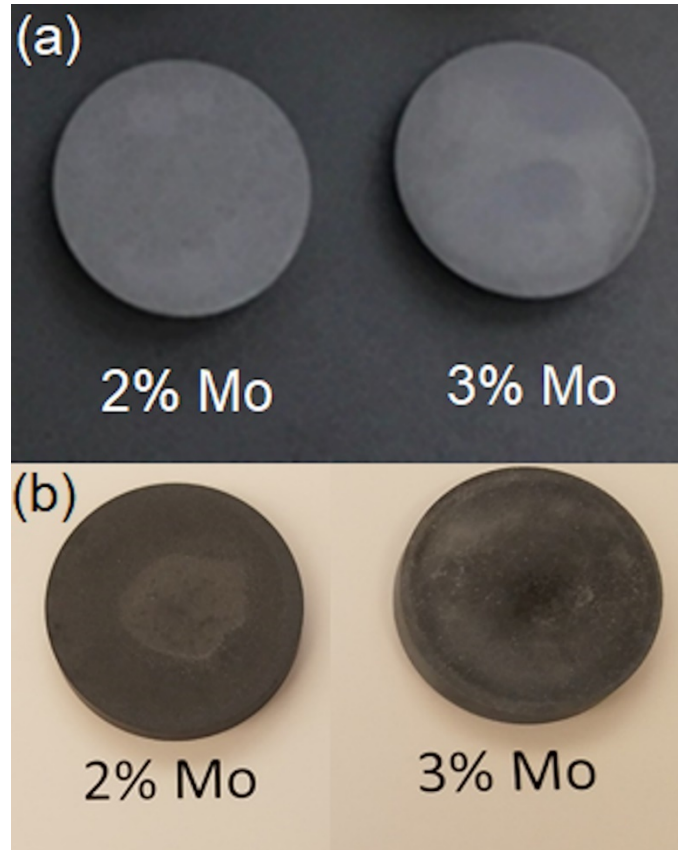


Figure 1. Examples of selected AlN:Mo samples prior to thermal cycling (a) and after 10 thermal cycles to 1000 °C in air (b).

3. Free Space Measurement Apparatus

A schematic of the experimental setup is shown in Figure 2. Free-space millimeter wave measurements were made using an Agilent Vector Network Analyzer (PNA N5222A) with OML Inc. 75-110 GHz extender heads (V10VNA2-T/R). The analyzer was first calibrated using through-reflect-line (TRL) calibration, which places the reference plane to the output WR-10 waveguides of the extender heads. Custom Millitech Gaussian horn antennas/lenses (GOA-10-120733A) with a focal length of 33 cm and Gaussian waist diameter (3.4cm) at 94 GHz were then attached to the waveguide output. After the TRL calibration and attaching the antennas, a gated-reflect-line (GRL) calibration placed the measurement reference plane at the front face of the AlN:Mo sample to be tested.⁸ At the sample, the Gaussian beam approximates a plane wave. Samples were approximately 5.3 cm in diameter and were held inside of a SiC sleeve, which was placed into the center of a Mellen tube furnace (Length: 31.75 cm Diameter: 15.24 cm). Alumina insulating foam with inner diameter of 6.75 cm was used to prevent excessive heat loss from the furnace. A picture of the setup is shown in Figure 3. Millimeter wave measurements were made with and without the alumina foam, and it was found that this foam had an insignificant contribution to the measurements.

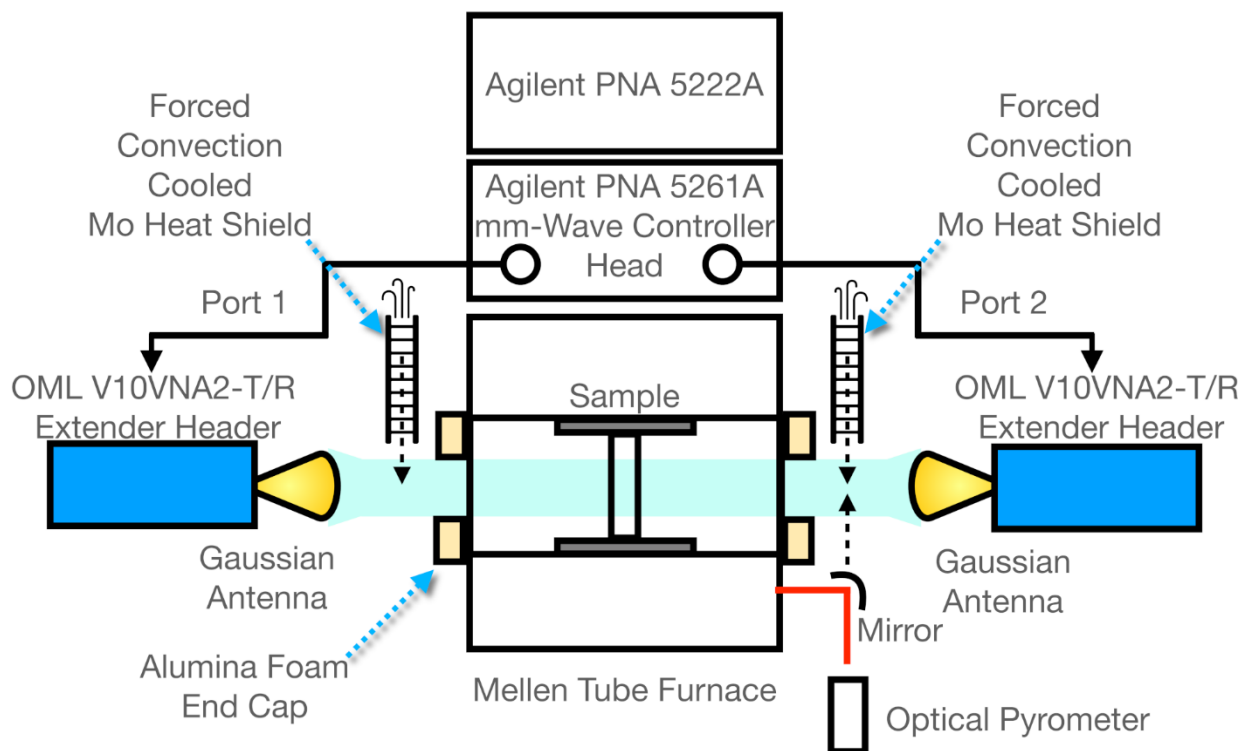


Figure 2. A schematic of the experimental setup. An enabling factor for achieving measurements at 1000 °C are the sliding Mo heat shields. The optical pyrometer allows for measurements of temperature at the center of the sample.

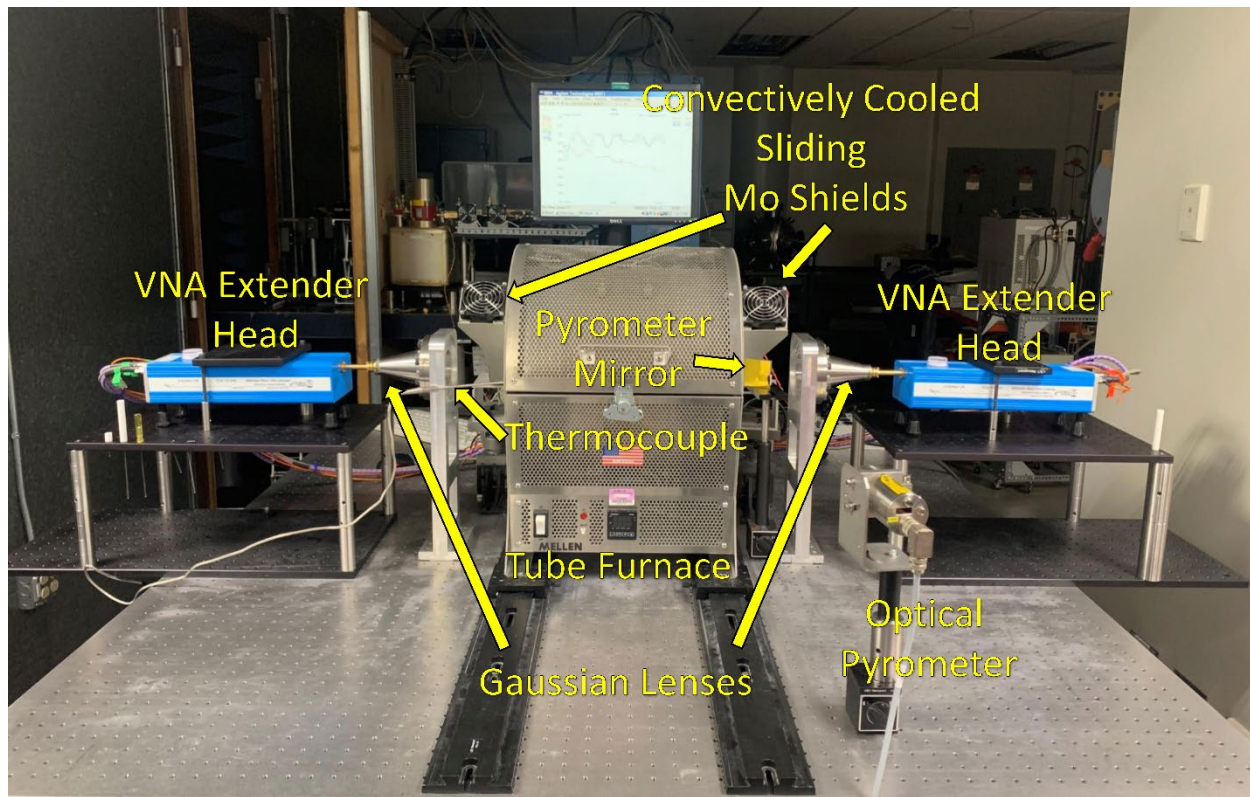


Figure 3. A photograph of the experimental setup for measuring the complex permittivity of samples up to 1000 °C.

In order to make accurate measurements up to 1000 °C, it was necessary to prevent heating of the antennas/lenses. Above about 550 °C, the samples and furnace began visibly radiating, acting as a near-perfect blackbody; the associated IR, in concert with convective heating, was found to be able to significantly raise the antenna/lens temperature. A picture of the sample at high temperature is shown in Figure 4. An increase in antenna/lens temperature can increase loss, change the focal length and spot size, and potentially distort the Gaussian beam – all of which will contribute to measurement inaccuracy. To prevent this, circular, mirror-polished Mo shields were attached to Al frames, which can be slid into place in front of the furnace apertures. Fans were attached behind the shields to keep them near room temperature, as shown in Figure 5.

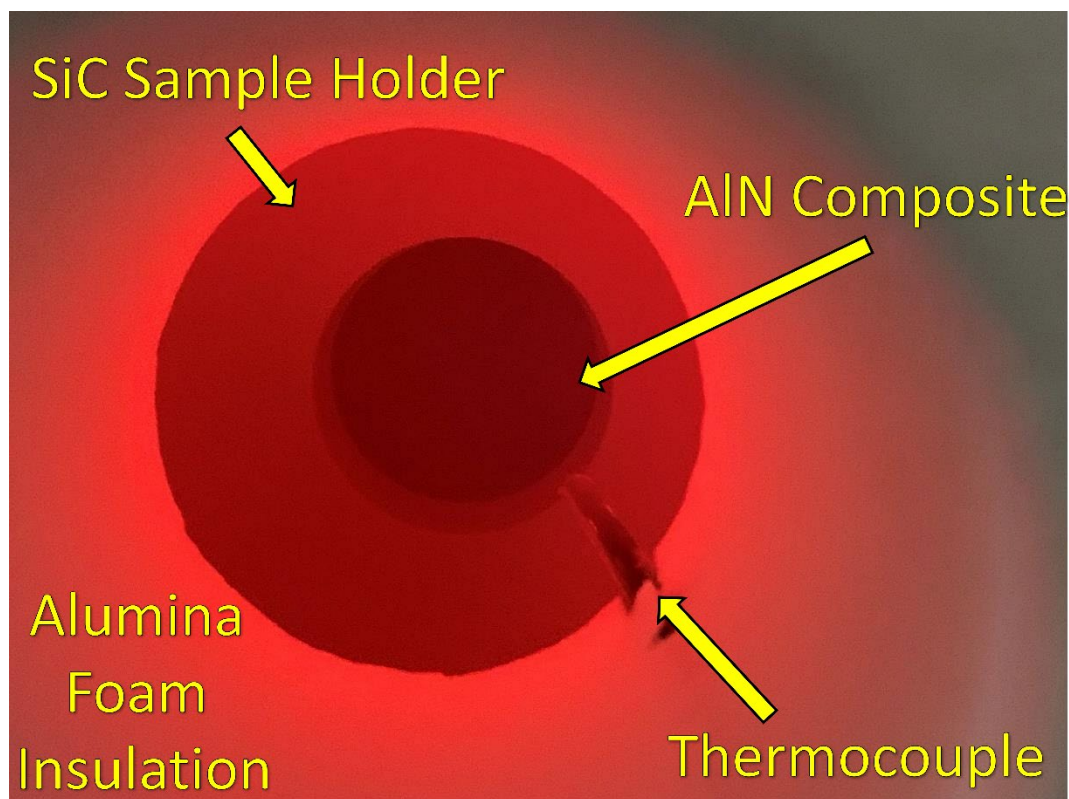


Figure 4. Shown here is a sample visibly radiating at a temperature of about 700 °C. A thermocouple gauge can be seen protruding from the alumina foam end cap and touching the surface of the SiC sample holder.

Temperature measurements were made using a LumaSense Technologies pyrometer (IGAR 6 RS485) and Omega thermocouples (TJ36-CAXL-316E); thermocouple accuracy is 2.2 °C or 0.75% of total temperature. At temperatures below 450 °C, the thermocouple was used exclusively for temperature measurements and was placed on the SiC sample holder. At temperatures above 450 °C, the SiC temperature can differ significantly (relative to the thermocouple accuracy) from that of the sample, which is located approximately 3.5 cm closer to the center of the furnace. Therefore, the pyrometer was used above 450 °C, while care was taken also to monitor the thermocouple gauge, which was placed on the opposite side of the furnace relative to the pyrometer. Multi-point temperature monitoring was necessary, as the air flow from the cooling fans can cause temperature imbalances on either side of the furnace – this technique allowed for on-the-spot placement corrections to balance the temperature. Temperature ramp rates were also kept to a few degrees per minute to help ensure temperature uniformity. To calibrate the pyrometer, multiple thermocouple gauges were placed on the sample and sample holder on each side, and data was taken up to 1000 °C. It was found through this technique that the temperature on opposite sides of the sample could differ by as much as ~10 °C around 450 °C. At very high temperature, this rose to as much as ~20 °C – this is larger than the accuracy limit ($\pm 7.5^\circ\text{C}$) of the thermocouple at high temperature and suggests some

level of non-uniform heating. We therefore estimate, conservatively, that the temperature accuracy below 600 °C is ± 5 °C and above 600 °C is ± 10 °C.

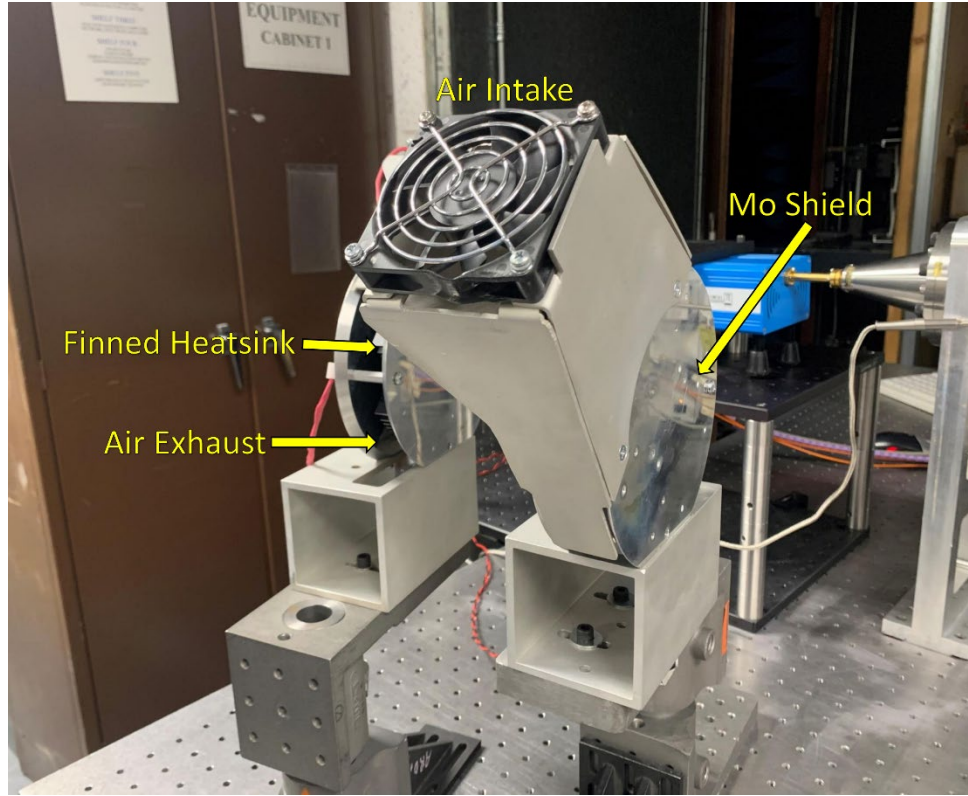


Figure 5. The convectively cooled Mo heat shields are shown here. The Mo is mirror polished, which allows reflection of infrared radiation back into the furnace.

4. Dielectric Property Extraction

To determine the dielectric properties of the measured samples, we followed an approach similar to the NIST technique.⁹ This technique involves fitting measured S-parameters to the S-parameter equations given by

$$S_{21} = R_1 R_2 \left[\frac{T(1-\Gamma^2)}{1-\Gamma^2 T^2} \right] \quad (0.1)$$

$$S_{11} = R_1^2 \left[\frac{\Gamma(1-T^2)}{1-\Gamma^2 T^2} \right], \quad (0.2)$$

where

$$T = \exp(-\gamma L) \quad (0.3)$$

$$\gamma = j \frac{\omega}{c} \epsilon_r \mu_r \quad (0.4)$$

$$\Gamma = \frac{\sqrt{\frac{\mu_r}{\epsilon_r}} - 1}{\sqrt{\frac{\mu_r}{\epsilon_r}} + 1} \quad (0.5)$$

$$R_1 = \exp(-\gamma_0 L_1) \quad (0.6)$$

$$R_2 = \exp(-\gamma_0 L_2) \quad (0.7)$$

$$\gamma_0 = j \frac{\omega}{c}. \quad (0.8)$$

L is the thickness of the dielectric sample, L_1 and L_2 are the distances between the measurement reference plane and the dielectric sample, ϵ_r and μ_r are the complex relative permittivity and permeability, ω is the angular frequency, c is the speed of light, and γ and γ_0 are the propagation constants in the dielectric and free space. In our setup, due to fixed antenna spacing, the reference plane is never exactly at the sample due to small differences in our calibration disk thickness and the sample thicknesses – this can be accounted for through use of equations 1.6 and 1.7. In the original work by NIST, S_{11} measurements were included in the fitting, but in our case, we found that measurements of S_{21} were significantly better than S_{11} uncertainty due to sample positioning/remounting, which is discussed further in the uncertainty analysis section. Particle swarm optimization was used to find, for each frequency point, the values of real and imaginary parts of permittivity that would best reproduce the experimental measurements of S_{21} phase and magnitude. It is likely that the variations in permittivity across the frequency band found during optimization are due to calibration and measurement uncertainties; a first order fit of the raw data was used to eliminate these variations – both the raw data and the first order fit are shown with error bars in Figure 6. Error bars are the result of uncertainty calculation given by NIST, which is discussed in more detail later. The S-parameters calculated using the optimized permittivity fit and first order fit are then shown in comparison to the measured S-parameters in Figure 7. Standard errors of the regressions for the optimized fit are found to be $\leq 10^{-4}$ for both S_{21} magnitude and phase.

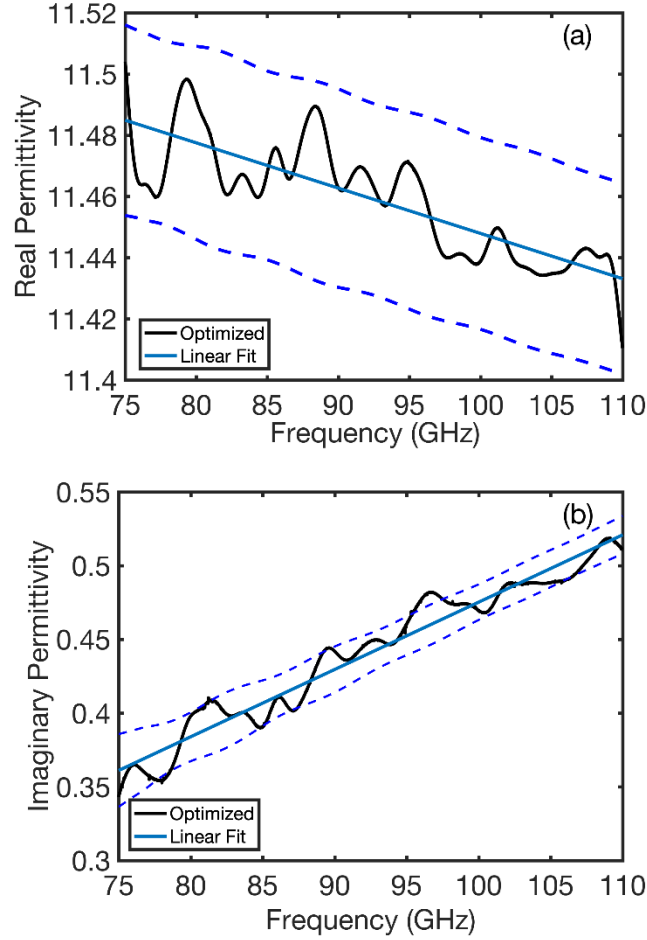
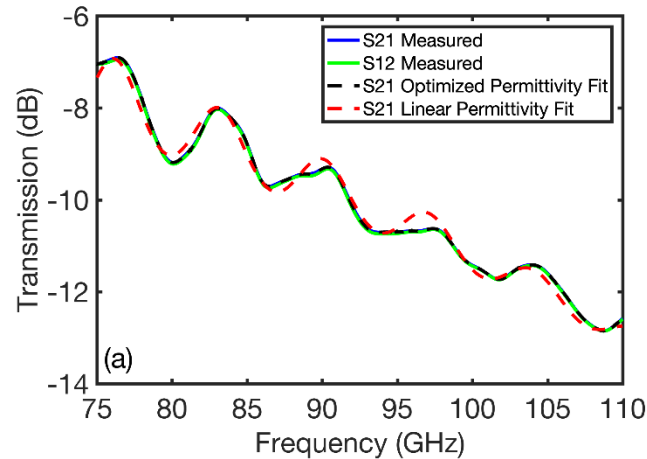


Figure 6. The real (a) and imaginary (b) parts of permittivity vs. frequency for AlN:Mo 3%. The black lines are the result of particle swarm optimization, used to extract permittivity from S_{21} . Oscillation geometry (size and shape) of the optimized line is dependent on specific calibration. A good alignment of standards/samples during calibration and measurements leads to small oscillations and higher precision measurement. Error bounds (dashed lines) are shown for the linear fit (blue lines).



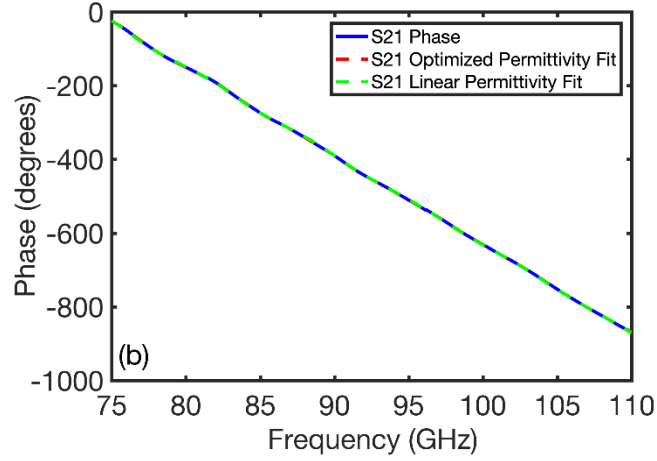


Figure 7. S_{21} and S_{12} magnitude (a) and S_{21} phase (b) vs. frequency are shown for AlN:Mo 3%. Dashed lines are reconstructed from the extracted permittivities using either particle swarm optimization or a linear fit to the optimization results. Both the optimized and linear fits of permittivity show good consistency with measurements.

The fitted and measured S_{11} data are shown in Figure 8 along with the data corresponding to S_{22} . It is noted that these reflection fits are not as consistent with the data when compared to S_{21} fits. This is owing to S_{11} 's higher sensitivity to sample alignment and placement. Displacements on the order of microns, determined through time domain analysis, can significantly change the shape of S_{11} peaks. When comparing the measured and calculated data, one may notice that the measured data shows multiple peaks, whereas the fitted data shows a single reflection maximum in many cases. This is due to additional interference from slight misalignment of the sample faces relative to where the metal reflector faces were positioned during the GRL calibration. Inevitably, if the metal is of different thickness than the sample, S_{11} or S_{22} will show additional peaks, since only one side can be aligned properly – in practice, neither side will be perfectly aligned, but it is visible from Figure 8 that the side of the sample facing port 1 was much closer to the original placement of the metal. The magnitude of the peaks can also strongly depend on the angle of the sample and the angle of the metal calibration disk.

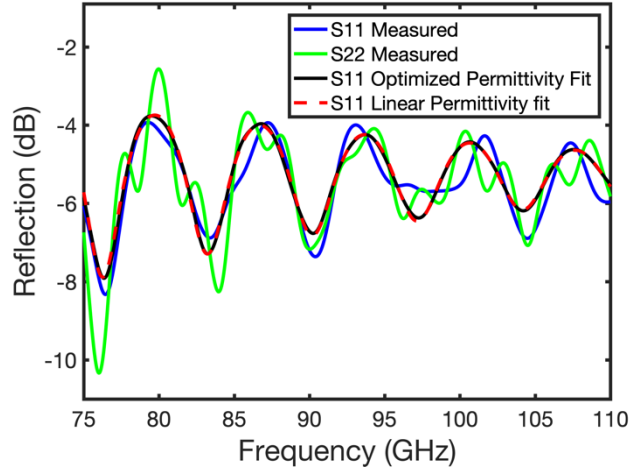


Figure 8. S_{11} and S_{22} vs. frequency are shown for AlN:Mo 3%. Differences between S_{11} , S_{22} , and the permittivity fit, which is based on S_{21} , arise primarily from imperfections in sample and calibration standard placement. These imperfections affect reflection more significantly than transmission.

5. Uncertainty Analysis

The most significant contributor to the S_{11} measurement errors is related to the sample holder. The sample holder is not fixed in place and allows for slight translation and rotation inside of the furnace. While these changes are not significantly different than other uncertainty sources for S_{21} , they can drastically change S_{11} . These sources of uncertainty affect both the calibration and measurement. In order to quantify the uncertainty arising from repositioning the samples, several samples were remounted 5 times and S_{21} measurements were taken. The standard deviation in S_{21} magnitude and phase across the 5 remounts and multiple samples was averaged across W-band to give a total remounting uncertainty. The following error propagation equation is used to determine total uncertainty in permittivity

$$\Delta\varepsilon = \sqrt{\left(\frac{\partial\varepsilon}{\partial|S_{21}|}(\Delta|S_{21}| + \Delta|S_{21fit}|)\right)^2 + \left(\frac{\partial\varepsilon}{\partial\theta}(\Delta\theta + \Delta\theta_{fit})\right)^2 + \left(\frac{\partial\varepsilon}{\partial L}\Delta L\right)^2} \quad (0.9)$$

where $\Delta|S_{21}|$ and $\Delta\theta$ are the uncertainties in S_{21} magnitude and phase, ΔL is the uncertainty in sample thickness, $\Delta|S_{21fit}|$ and $\Delta\theta_{fit}$ are the respective standard errors of regression in S_{21} magnitude and S_{21} phase found from comparing the S_{21} data from the linear fit of permittivity to the measured S_{21} . ΔL is given by the largest standard deviation in our measurement of sample thicknesses (10 measurements per sample). $\Delta\theta$ is given by the remounting uncertainty in phase. $\Delta|S_{21}|$ is given by the remounting uncertainty in quadrature with the measurement uncertainty from the VNA after GRL calibration. The difference between the measured S_{21} and true S_{21} is determined through circuit/signal flow graph analysis of the VNA, assuming standard 12 term error sources, and is given by ^{10,11}

$$S_{21measured} = E_D + E_{TT} \frac{S_{21}}{1 - E_S S_{11} - E_L S_{22} + E_S E_L (S_{11} S_{22} - S_{21} S_{12})} \quad (0.10)$$

where E_D is the error term for directivity, E_{TT} is the error term for transmission tracking, E_S is the error term for source match and E_L is the error term for load match. We determined the magnitude of the difference between measured S-parameters and hypothetical S-parameters and used this as our uncertainty from the VNA. The residual error terms after the TRL calibration are given by the VNA and were used in the uncertainty analysis, with the exception of load and source match. Residual load and source match errors are, by far, the most significant contributors of error, and these are manually determined after the GRL calibration. To find the residual source and load match errors, the reflections due to the sending/receiving antennas were isolated in time domain. These gated time-domain reflections were then transformed back to frequency domain, which enabled determination of their frequency dependent contribution to S-parameter error. The magnitude of the errors due to source and load match are expected to be high due to relatively large reflections from our antennas, which consist of aluminum housings and quartz lenses. It was possible to reduce these errors by using antenna lenses made of less reflective material (polymer/rexolite), but these antennas are not suitable for high temperature measurements. However, reducing errors as a result of the antennas would not significantly change the measurement, as the measurement uncertainty due to remounting and that arising from our linear fit of permittivity were of similar magnitude. The fact that the uncertainty due to the permittivity fit is similar to our other sources of uncertainty is perhaps not a coincidence; the uncertainty as a result of remounting as well as VNA error play a role in the calibration and could contribute to S-parameter fluctuations, which deviate from those produced by a quasi-linearly varying permittivity. Other sources of error which may contribute include changes to the gaussian beam as a result of the presence of the sample (e.g., focusing/defocusing, diffraction) and the non-uniform focal length of the lenses with frequency, both of which can lead to deviations with respect to equations 1.1-1.2 which assume plane waves; the gaussian beam waves which reach the antennas will also not couple as well as the calibrated beams due to the same effects, which could lead, for instance, to a change in phase or a decrease in measured transmission magnitude.

Results and Discussion

Data from measurements of the thermally cycled AlN:Mo sample set are plotted in Figure 9 and Figure 10. Figures 9 (a) – (f) provide plots for the real portion of the permittivity and Figures 10 (a) – (f) provide plots for the imaginary portion of the permittivity for temperatures ranging from 25 °C to 1000 °C. Both sets of plots also provide data from the AlN:Mo sample series prior to thermal cycling at temperatures ranging from 25 °C to 550 °C, for comparison.

With the exception of the 4 vol% Mo sample, the measured differences in complex permittivity before and after thermal cycling are relatively minor, indicating stability of material properties influencing mm-wave absorption in environments of interest for electromagnetic heat exchanger applications. The thermally cycled 4 vol% Mo sample data indicate reductions in both real and imaginary permittivity from the un-cycled samples in the 25 °C to 550 °C temperature range. Observed reductions in real permittivity range from 1.1% to 1.8%, and reductions in

imaginary permittivity range from 3.8% to 5.7%. Further investigation, including microstructural analysis, is required to understand if these changes in permittivity are potentially attributable to material changes in the 4 vol% Mo due to the thermal cycling process.

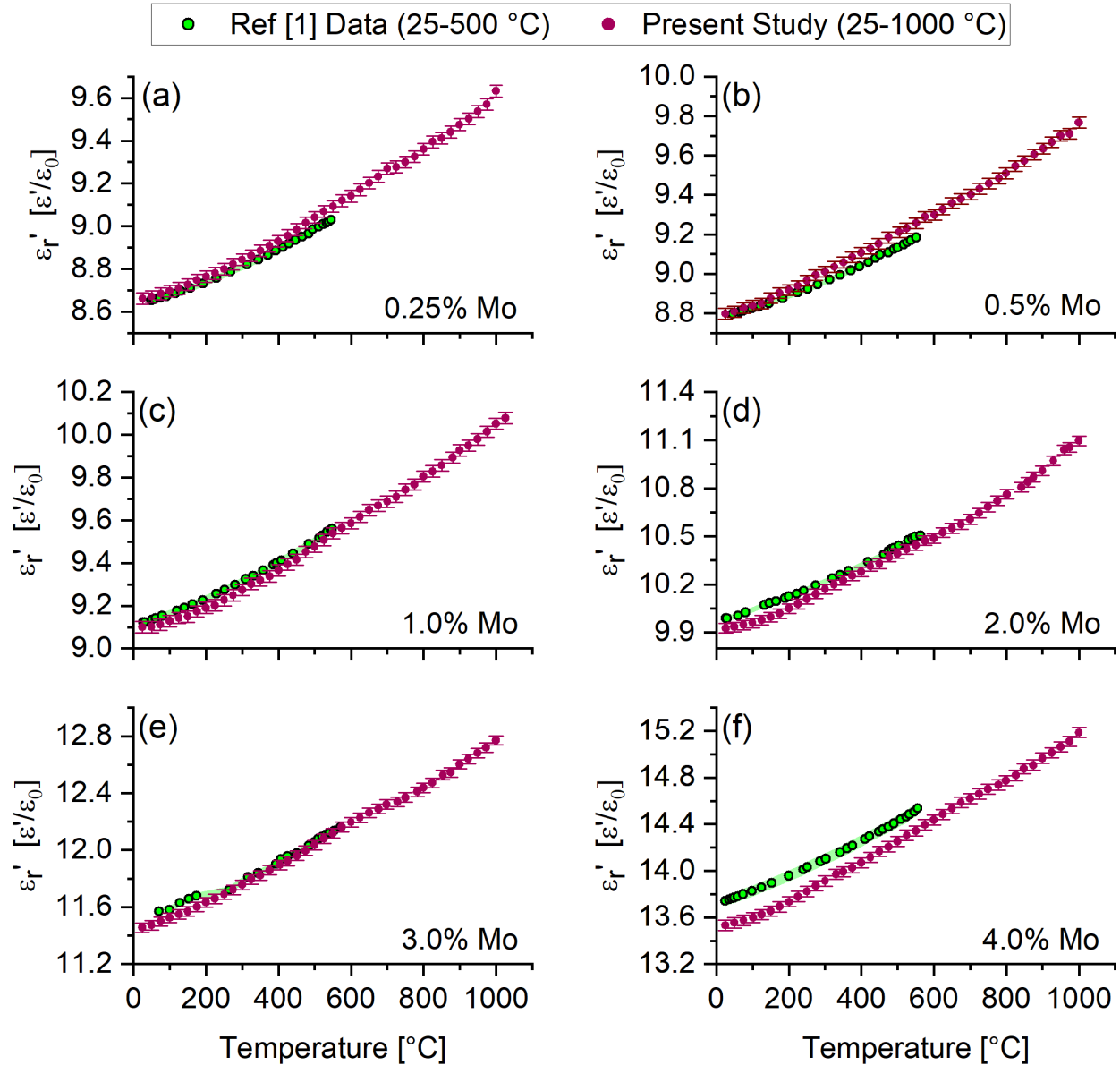


Figure 9. Measured values of the real permittivity of AlN:Mo as a function of temperature before (green circles) and after (magenta circles) 10 heat cycles to 1000 °C. Data for Mo vol% concentrations of 0.25 (a), 0.5 (b), 1.0 (c), 2.0 (d), 3.0 (e), and 4.0 (f) are provided.

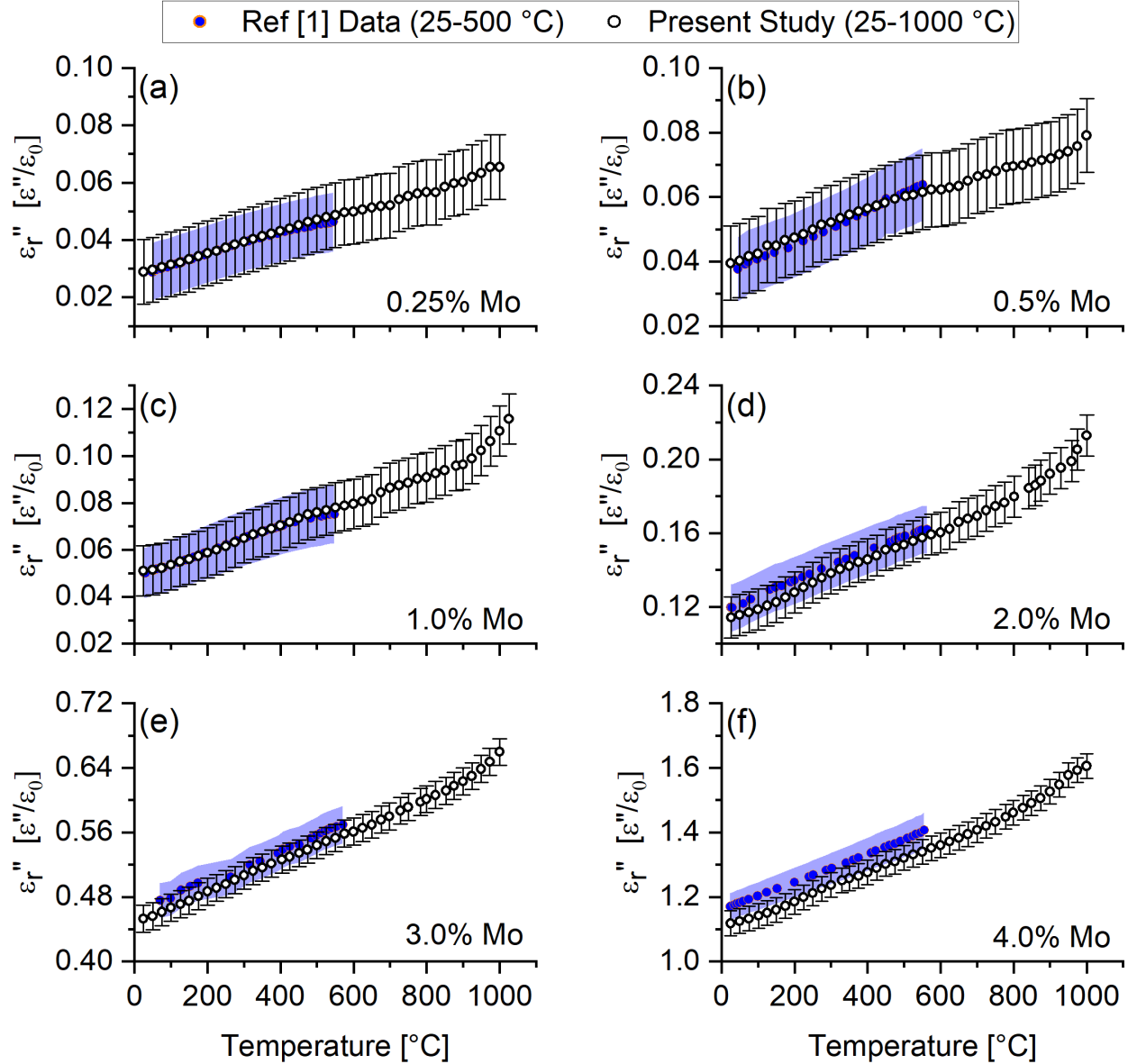


Figure 10. Measured values of the imaginary part of permittivity of AlN:Mo as a function of temperature before (green circles) and after (magenta circles) 10 heat cycles to 1000 °C. Data for Mo vol% concentrations of 0.25 (a), 0.5 (b), 1.0 (c), 2.0 (d), 3.0 (e), and 4.0 (f) are provided.

Summary

Modifications to a high-temperature, free-space, permittivity measurement system have extended the maximum useable temperature from 550 °C to over 1000 °C. Data reduction and sources for error for this setup were addressed. This system was used to characterize a set of six AlN:Mo ceramic-metal composites (0.25%, 0.5%, 1.0%, 2.0%, 3.0% and 4.0%, by volume) under evaluation for use as susceptor materials in electromagnetic heat exchangers. With the exception of the highest concentration Mo sample (4 vol% Mo), measured real and imaginary permittivity of the thermally cycled samples showed little change from previously published

measurements performed in the range of 25-550 °C prior to thermal cycling. The 4 vol% Mo sample exhibited reductions in real permittivity (1.1% to 1.8%) and imaginary permittivity (3.8% to 5.7%) in the 25-550 °C regime. Further analysis is required to understand possible links between the thermal cycling process and potential material changes in the 4 vol% Mo sample.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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