Development of a novel instrument for microwave dielectric thermal analysis

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The advantages of microwave heating in industrial processing are becoming more widely appreciated and the technique is of increasing commercial significance. However, knowledge of a material's dielectric properties as a function of temperature is of considerable importance as they determine the efficiency with which the material converts microwave energy into heat. This article describes the development of a novel instrument for a new form of thermal analysis, microwave dielectric thermal analysis (MDTA) in which the sample is heated not conventionally but by microwaves, while its dielectric properties at microwave frequencies are determined quasisimultaneously using a network analyzer. A plot of the dielectric properties against temperature then gives the MDTA curve. The fundamental principle underlying the use of MDTA is that not only do a material's dielectric properties (both the real and imaginary parts of the complex permittivity) alter (generally smoothly) as a function of temperature but dramatic differences can be found when chemical or physical changes occur. MDTA measures the sample's dielectric properties as a function of temperature before, during, and after the chemical and/or physical changes occurring as it is heated in the microwave field and thus provides a unique way of studying them. Furthermore, due to the quasisimultaneous nature of the measurements, MDTA can also make a valuable contribution to the investigation of the so-called "microwave effect" anomalies that occur when certain materials are heated in a microwave field. We show that the technique can be used to study a wide range of thermal transformations, including solid-solid phase changes, melting, and chemical reactions, e.g., dehydration, via the complex permittivity-temperature profiles generated in MDTA. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2179412]

I. INTRODUCTION

Microwave heating has a diverse range of applications and impacts in domestic, industrial, scientific, and medical sectors.[1–4] The extensive use of microwave energy in heating is due to the significant advantages it provides over conventional methods.[5] These include the potential for highly uniform heating, the ability to achieve exceptionally rapid heating rates in certain materials, and improved levels of process control over conventionally heated systems.

Fundamental to the processing of materials using microwave radiation is the measurement of a material's permittivity and the ability to monitor its variation with temperature. With the increased use of microwave radiation in materials processing, a number of workers have developed several different approaches in measuring permittivity as a function of temperature. The ultimate aim is to be able to simultaneously heat the sample with microwaves and detect the changes in permittivity that result. The problem to be overcome is that the power levels required for heating (kW) and measurement (mW) differ by several orders of magnitude so the sensitive measurement equipment requires complete isolation from the high powers used to heat samples.

The measurement of temperature in this type of device is significantly more difficult than in standard microwave thermal analysis equipment, where grounded thermocouples have been demonstrated to provide reliable temperature measurement.[6] The problem is due to perturbations of the electromagnetic field by conductors, such as thermocouples, which must be avoided in permittivity measurements based on the perturbation of a resonant cavity. Pyrometers, while having a wide operating temperature range, can only indicate surface temperatures.

However, fiber optic probes, which have negligible interaction with microwave radiation, are contact temperature sensing devices and are ideally suited for use in microwave dielectric thermal analysis (MDTA) as they can be placed in the sample.

Different strategies have been adopted by previous researchers in their attempts to overcome these problems. One

of the most common methods is to heat the sample in a separate furnace and then quickly transfer it to a resonant microwave cavity where the perturbation of the resonant frequency is used to determine its dielectric properties.[7,8] Charreyre *et al.*[9] have instead developed a system in which the sample is moved out of the electromagnetic field only for the purpose of temperature measurement. Rather than using low power microwaves to determine a perturbation of the cavity, these authors used a movable short circuit to terminate the cavity, which is then moved to ensure the cavity remains in resonance. Its displacement is then used to determine the real and imaginary parts of the complex permittivity. The accuracy of the measurement will inevitably be a function of measurements of the deviation of the short circuit and the time delays associated with removing the sample for temperature measurement. Ollivon *et al.*[10] used a system in which the sample was placed in a resonant cavity, with microwave power being supplied by a variable frequency microwave source. If the resonant frequency of the cavity changes as a result of variations in the material's dielectric constants, then the frequency of the applied radiation can be changed to bring the system back to resonance. From this frequency shift, the changes in ε' and ε'' can be determined. The limitation of this technique is that it is only capable of working with low microwave powers, typically 6 W, and hence only permits the study of materials that are strong absorbers of microwave energy.

A relatively simple, low cost device has been described by Moreau *et al.*[11] who used a six port reflectometer in conjunction with a series of diode detectors to make measurements. The system requires extensive calibration and the determination of the sample's dielectric constant is based on several assumptions.

We felt that an alternative approach might address some of the issues mentioned above. Following our earlier development on microwave thermal analysis,[6] this article describes the new technique of MDTA in which the dielectric properties of a material are measured as a function of temperature as it is heated in a microwave field. It differs from other methods for measuring dielectric properties as a function of temperature[7] as we use both a network analyzer and direct temperature measurement, with the sample remaining in the cavity throughout the experiment. MDTA uses the changes in a material's dielectric properties that occur as it undergoes thermally induced transformations to detect the events, thus making it a valuable addition to the existing range of thermoanalytical techniques. MDTA also provides a new means of studying systems in which microwave heating has been observed to induce reactions at apparently lower temperatures than found with conventional heating, the so-called "microwave anomaly" effect.

II. THEORY OF MICROWAVE HEATING

Microwave heating is related to the dielectric properties of the interacting material.[1,2,5,12,13] These are the imaginary and real components of the complex permittivity and their ratio, the loss tangent (tan δ). The greater a material's loss tangent is, the greater will be the heating rate in a given microwave field. A material's dielectric properties vary with temperature and, except at very high temperatures, this change is relatively minor.

However, when a material undergoes a chemical or even, in some cases, a simple phase change, there can be dramatic alterations in its dielectric properties. From the perspective of materials processing, large increases in the loss tangent can cause severe process control problems, with the potential for thermal runaway. Therefore, any technique that provides information regarding the change of a material's dielectric properties as a function of temperature will be of considerable use to workers in the area of materials processing using microwave energy.

Microwave heating relies on the ability of an applied electric field to polarize the charges in an insulating material and the inability of the polarization to follow the high speed reversals of the electric field. The lag of the polarization vector **P** with the electric field vector **E** results to a current $\partial P/\partial t$, a component of which results in the dissipation of power as thermal energy within the material. Thus the dielectric properties of a material dictate the efficiency with which it will be heated in a microwave field. In addition to this, conduction effects may also contribute to the heating of the material.

The total current density induced in a material of relative complex permittivity ε_r^* ($\varepsilon_r^* = \varepsilon_r' - j\varepsilon_r''$) when an alternating electric field, $E_0 e^{j\omega t}$, is applied is given by Maxwell's equations:

$$\nabla \times H = J = \sigma E + j\omega\varepsilon_0\varepsilon_r^* E, \tag{1}$$

$$J = j\omega\varepsilon_0\left(\varepsilon_r' - j\left(\frac{\sigma}{\omega\varepsilon_0} + \varepsilon_r''\right)\right)E = j\omega\varepsilon_0\varepsilon_{r\,\mathrm{eff}}^* E, \tag{2}$$

where $\varepsilon_{r\,\mathrm{eff}}^* = \varepsilon_r' - j\varepsilon_{r\,\mathrm{eff}}'' \cdot \varepsilon_{r\,\mathrm{eff}}^*$ is the effective relative permittivity, the parameter we measure. The real part, i.e., the dielectric constant (ε_r'), represents the stored energy and the imaginary term ($\varepsilon_{r\,\mathrm{eff}}''$) accounts for the total dielectric loss in the material. Many mechanisms such as dipolar, atomic, electronic, and interfacial [Maxwell-Wagner (MW)] polarizations and the dc conductivity effect could contribute in theory to the effective loss. The MW polarization effect is due to the interaction of microwaves with the charges which can be found at the interface between two materials. However, in the microwave frequency range, dipolar and MW polarizations and dc conductivity are usually the dominant contributing factors.

The loss mechanism is generally represented by the loss tangent, tan δ_{eff}, which is given by

$$\tan\delta_{\mathrm{eff}} = \frac{\varepsilon_{r\,\mathrm{eff}}''}{\varepsilon_r'}. \tag{3}$$

The fundamental relationship governing microwave heating is[13]

$$P = \omega\varepsilon_0\varepsilon_r' \tan\delta_{\mathrm{eff}} E^2, \tag{4}$$

where P is the power dissipation per unit volume in a material, E is the electric field in the material, and ω is the angular frequency ($\omega = 2\pi f$, where f is the frequency). From (4),

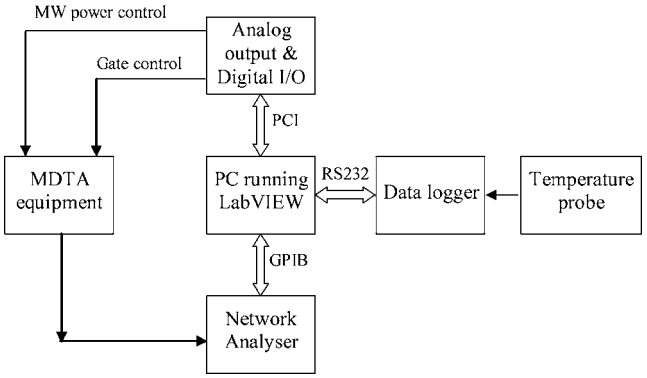

FIG. 1. Schematic of the system.

the rate of rise of temperature when the material is exposed to a microwave field can be expressed as

$$\frac{dT}{dt} = \frac{0.556 \times 10^{-10} \varepsilon''_{r\,\mathrm{eff}} f E^2}{\rho c_p} \quad (^\circ\mathrm{C\ s^{-1}}), \tag{5}$$

where ρ, c_p, and $\varepsilon''_{r\,\mathrm{eff}}$ are the density, the specific heat capacity, and the loss part of the permittivity of the material, respectively.

III. DIELECTRIC MEASUREMENT THEORY

The complex permittivity of the sample is determined using the cavity perturbation method.[14] Initially, an empty sample holder tube is placed inside the waveguide and the resonant frequency f_{sh} and quality factor Q_{sh} of the cavity are noted. The same parameters are again recorded when the sample tube is filled with a known volume of water to give the values f_w and Q_w. When a sample of equal volume to that of the water previously measured is used, the cavity parameters f_s and Q_s can be obtained. As the relative complex permittivity of water ($\varepsilon^*_{rw} = \varepsilon'_{rw} - j\varepsilon''_{rw}$) at microwave frequencies is known, comparison of the equations corresponding to water and the sample gives the effective relative complex permittivity of the sample, $\varepsilon^*_{r\,\mathrm{eff}} = \varepsilon'_r - j\varepsilon''_{r\,\mathrm{eff}}$, where

$$\varepsilon'_r = 1 + (\varepsilon'_{rw} - 1)\frac{f_{\mathrm{sh}} - f_s}{f_{\mathrm{sh}} - f_w}\frac{f_w}{f_s}, \tag{6}$$

$$\varepsilon''_{r\,\mathrm{eff}} = \varepsilon''_{rw}\frac{Q_{\mathrm{sh}} - Q_s}{Q_{\mathrm{sh}} - Q_w}\frac{Q_w}{Q_s}. \tag{7}$$

The parameters f_{sh}, f_w, Q_{sh}, and Q_w are obtained prior to commencing the experiment and stored. At each measurement cycle, the program acquires the parameters f_s and Q_s from the network analyzer. The values of ε'_r (dielectric constant) and $\varepsilon''_{r\,\mathrm{eff}}$ (loss term) are then calculated using Eqs. (6) and (7) and stored in the computer. All the data we present here have been measured at 2.03 GHz.

IV. INSTRUMENTATION

Schematic diagrams of the MDTA instrument and the measurement and control systems are shown in Figs. 1–3. The function and operation of each of the modules are detailed in the following sections.

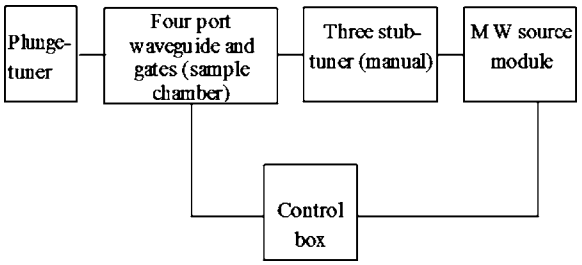

FIG. 2. Schematic of the MDTA equipment.

A. Microwave generator and heating/measurement cavity

The main function of this section of the instrument is to provide a cavity that will permit single mode microwave heating while giving protection to the sensitive network analyzer (NWA) used to make measurements of the sample's dielectric properties. The system operates by cycling between microwave heating and dielectric measurements.

The sample is mounted in a section of a 9A waveguide which has two pairs of isolation gates, one of each pair being shown in Fig. 3. One pair of these, situated in the long waveguide, allows heating to take place while the other, which is located in a further short section of the waveguide (again 9A) at each side of the sample chamber, permits the propagation of the low power microwave energy supplied by the network analyzer. Each of these sections is fitted with specially designed and critically placed irises. The volume contained by the gates comprises the sample chamber.

In the heating part of the cycle, the measurement ports are first isolated by closing both measurement isolation gates before opening the heating gates. Microwave energy can then be applied to the sample from the switch mode power supply (maximum of 1 kW). The propagation of the microwave field is via the TE_{01} mode. To obtain the most efficient heating, the cavity is tuned to attain the maximum E field at the point where the sample is located by using adjustable plunge and three-stub tuners.

Optimum tuning is assessed from the dc signal produced from an E-field probe connected to a cathode ray oscilloscope (CRO). The probe is positioned at a distance of $\lambda/2$ from the sample and therefore the maximum signal displayed on the CRO is indicative of the maximum in the E field at the sample position. The power supply is protected from the adverse effects of high levels of reflected power by the inclu-

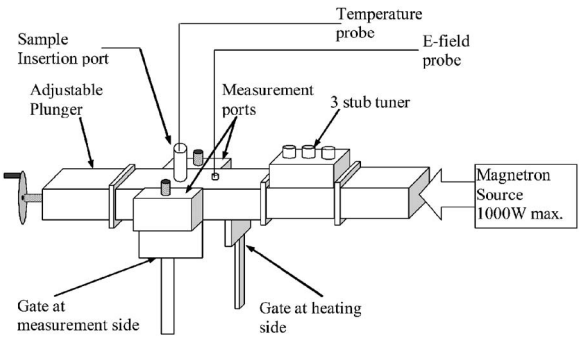

FIG. 3. MDTA equipment.

sion of a circulator and dummy load. Meters are fitted such that values for both the forward and reflected powers are available to the operator at anytime during the experiment.

To measure a material's dielectric parameters, the microwave power is first turned off, the heating ports isolated by closing (raising) their gates, and the gates on the measurement ports lowered to the open position. The NWA can then be used to measure the sample's dielectric properties (see Sec. III). The isolation gates are actuated by compressed air ($\approx$3 bars). The equipment is fitted with safety relays that prevent both sets of gates from being simultaneously in the open position. This is necessary as exposing the NWA to the high power microwave energy used for the heating process would result in significant damage. The position of the isolation gates can be controlled manually or, more usually, via the software using the digital outputs from the analog to digital converter (ADC)/digital to analog converter (DAC) (see Sec. IV B).

A fluoroptic temperature sensor (Sec. IV C) is inserted into the sample to provide accurate temperature measurement and so permit changes of the sample's dielectric properties to be measured as a function of temperature.

B. ADC/DAC

The ADC/DAC card, PCI-DDA04/12, has four analog output channels and 48 digital input (I)/output (O) lines. It mainly serves the following purposes:

(a) Controlling the gates at the measurement and heating ports using digital output lines. The digital signals control solid state relays (SSRs), which in turn control the 24 V supply to the pneumatic valves which actuate the gates. Each gate is controlled by two serial SSRs for increased protection of the network analyzer.
(b) Checking the interlock status of the microwave generator using the digital input lines. Via a series of switches, the software checks that the four gates have been opened or closed, as appropriate, in order to safeguard against the possibility of gate failure damaging the NWA. Each gate is provided with two switches in case of failure of one of them.
(c) Controlling the microwave power via an analog output voltage (0–10 V). The resolution of this output is 12 bits and 10 V output gives maximum microwave power (1 kW).

C. Temperature measurement

A fluoroptic thermometer, interfaced with the computer through the RS 232 serial bus, is employed for temperatures up to 295 °C. This is a nonmetallic immersion probe (Luxtron STF model) giving accurate temperature readings (±0.2 °C) and a response time of 250 ms. It is electrically nonconductive and immune to electromagnetic interference. The tip of the probe has a diameter of ~0.8 mm and the perturbation it imposes on the field is small. Measurements indicate that the probe causes changes in the empty cavity resonance frequency of only $(3.8\times10^{-3})\%$ and in the quality factor of 0.31%.

For higher temperatures an infrared pyrometer is used (Raynger MX4 high performance infrared thermometer manufactured by Raytek with range of −30–900 °C and accuracy of ±1.5 °C).

D. Sample holder

The sample cell is constructed from silica glass, has an inner diameter of 4 mm, and is filled in order to produce a sample bed depth of 2 cm. The cell is inserted into the measurement cavity through the sample port along the transverse direction as shown in Fig. 3.

E. Validation of the MDTA cavity

The relative complex permittivity parameters of the sample of SiC used in this work were measured using a conventional rectangular cavity with the standard cavity perturbation technique and found to be $\varepsilon^*_{r\,\mathrm{eff}}=9.22-j0.88$ at 20 °C. Using the same method, but with the MDTA cavity, we found $\varepsilon^*_{r\,\mathrm{eff}}=9.14-j0.73$. The small discrepancies can be attributed to the unconventional nature of the cavity used in the MDTA equipment which has to serve also as part of the heating cavity.

V. OPERATION OF THE MDTA INSTRUMENT

The complex permittivity data are calculated employing the cavity perturbation technique using a NWA which is interfaced to the single mode (TE_{01}) microwave heating system. The instrument is operated under a control software written using LABVIEW, which provides control of all the components.

A. Heating/measurement cycle and gate operation

In a typical experiment the instrument is set to the heating mode for 57 s, during which the heating gates are open and the NWA measurement gates closed. At the end of this period the power is switched off, the heating line gates closed (ca. 1 s), and a delay of 1 s is then used as a precautionary measure to ensure the gate changes have had time to occur. The measurement gates are then opened (ca. 1 s) and three sets of dielectric readings are made. Each takes ca. 30 ms and 50 ms is allowed to elapse between them. The measurement gates are then closed (ca. 1 s), the heating gates opened (ca. 1 s), and the power applied. Due to minor limitations in the current generator, there is a short delay of around 2.5 s as the power builds up to the level required to recommence heating. With these settings, the complete cycle takes around 8 s.

It should be noted that although the sample may cool a few degrees during the short time the heating is off, as the temperature is measured every 0.5 s, the temperature measurement is virtually simultaneous with the NWA readings. The instrument was designed to operate in either of the two heating modes described below.

B. Constant power heating

In this mode the desired power level is set prior to commencing the heating program. When the program is activated

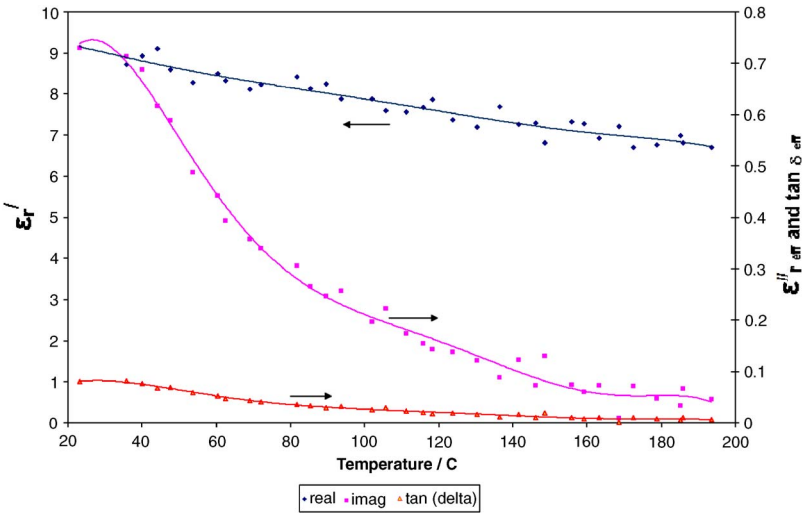

FIG. 4. (Color online) Variation of dielectric properties of SiC with respect to temperature.

a software window is opened that asks the operator to check the status of air, water supply, etc. On selecting "YES," the program continues and sets the NWA to the desired parameters (S_{21} or S_{11}), format (magnitude, phase, etc.), power sweeping mode, and other basic settings. The heating gate is then set to open and the power increased to the preset level. At predetermined time intervals the power is set to zero, the heating gates closed, and the measurement gates opened.

Measurement is then performed using the NWA. Once this has been done, the measurement ports are closed and the heating cycle recommenced. The process of heating and measurement continues until a preset condition (either time or maximum temperature) is achieved.

C. Linear heating

The basic operation of this mode is similar to that described above and differs only in the variation of the microwave power during the heating regime. In this mode it is possible to select a desired heating rate, typically between 1 and 50 C min^{-1} and the program then varies the microwave power accordingly. Initially, a power of 100 W is applied and, at 500 ms intervals, the current heating rate is compared with desired heating rate. The proportional, integral and derivative (PID) algorithm in the program then calculates the error in heating rate and adjusts the power to keep the rate the same as the set value. For both the above heating regimes the facility for initial drying/heating of the sample at a chosen preset temperature is provided.

The program also allows manual override of the microwave heating power which may be needed when the transition occurring is so vigorous as to cause the heating rate to deviate significantly from the set value.

VI. SAMPLE PREPARATION

While some samples can be studied in their pure state, others benefit from dilution with an inert material. Instances where the use of a diluent proved to be beneficial are outlined below:

(a) Some materials have an exceptionally low loss tangent and hence do not couple effectively with the microwaves. Mixing the sample with a good microwave absorber, called a "susceptor," overcomes the heating problem and does not interfere with measurement of the material's dielectric properties and the subsequent detection of any thermally induced transitions.

(b) Some materials that undergo solid-liquid phase transitions have a tendency to stick to the temperature probe. It was found that this can often be avoided by mixing with an inert diluent.

(c) Some materials were found to undergo large changes in their dielectric properties during thermal transformations which can make temperature control challenging. This problem can be overcome without interfering with the measurements by using an inert diluent.

In the present work, all the samples were mixed with silicon carbide (SiC) (Aldrich 450 mesh). SiC is physically stable and chemically inert over a wide range of temperatures. Each sample was mixed with SiC in appropriate proportions and finely ground to get uniform mixing. The proportions of SiC to the different samples are, by weight. Stearic acid: 10:1, zinc acetate: 10:0.5, and silver iodide: 10:2. All future references to these samples refer to the above mixtures.

VII. EXPERIMENTAL RESULTS

In this article the potential usefulness of the MDTA instrument is illustrated using three types of thermal transformation, namely solid-solid phase changes, dehydration, and melting.

This is not meant to be an exhaustive list as clearly MDTA can be used to monitor and study a wide range of physical and chemical transformations.

SiC has no physical or chemical changes over the temperature range studied but was examined to provide data to illustrate the variation of the dielectric parameters which can be found as a material is heated (Fig. 4). It can be seen that the dielectric constant, ε_r', slowly and steadily decreases with temperature, while the imaginary part of the relative complex permittivity, $\varepsilon_{r\,\text{eff}}''$, only appears to show a more rapid de-

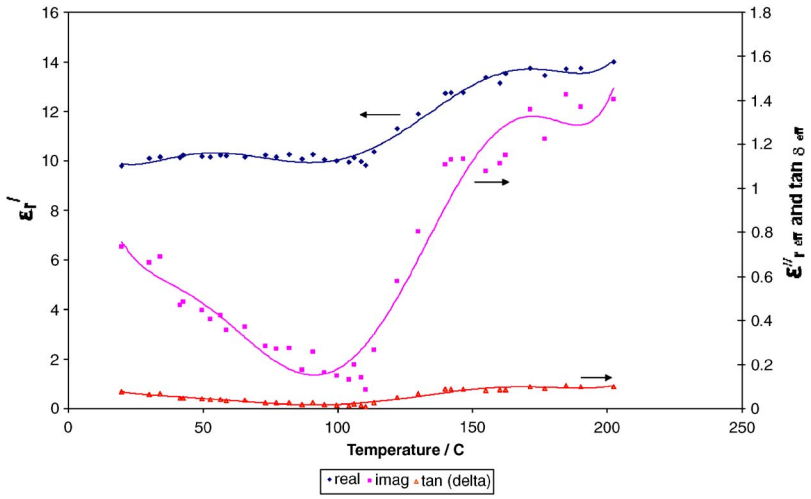

FIG. 5. (Color online) Variation of dielectric properties of AgI with respect to temperature.

crease with rising temperature due to the scale used. tan δ_{eff} shows a gradual decrease with increasing temperature,

A. Solid-solid phase change

However, in the case of AgI it can be seen that the dielectric constant varies only slightly with temperature until 100 °C is reached (Fig. 5), after which it changes fairly sharply until leveling off at approximately 160 °C. The value of $\varepsilon''_{r\,\text{eff}}$ for AgI as it underwent its phase transition changed even more dramatically and provides an excellent means of determining the phase transition. The changes in tan δ_{eff} again broadly mirror those of the other two parameters.

The region of 100–160 °C corresponds to the phase transition β-AgI to α-AgI. The phase transition temperature (T_c) can be taken as the center point of the transition region, 130 °C, which is a value lower by 17 °C than the literature value of 147 °C.[15] A decrease in the phase transition temperature in AgI under conditions of microwave heating has previously been reported by Robb *et al.*[15] who reported a lowering of the phase change temperature of more than 30 °C. Their study involved monitoring the phase transition by performing *in situ* x-ray diffraction measurements while using microwave heating.

They attributed the lowering of the phase transition temperature to multiphonon interactions with the microwaves and low-lying transverse optic modes. The results we report are reasonably consistent with those of Robb *et al.* and the apparent lowering of the transition temperature might well suggest a microwave effect. However, further work would be needed to verify the possibility, but this is beyond the scope of the current instrument development article.

B. Dehydration

Dehydrations are a type of thermal transition of commercial significance that are widely studied using conventional thermal analysis techniques. The dehydration of zinc acetate was used to illustrate the application of MDTA to this important class of chemical process.

The dielectric parameters for zinc acetate on heating are shown in Fig. 6. It can be seen that ε'_r initially decreased until ca. 93 °C, then rose rapidly, attaining a maximum value at 113 °C, after which it fell slightly but maintained a value significantly higher than that of the hydrated material. The results for $\varepsilon''_{r\,\text{eff}}$ show a corresponding peak, as does the tan δ_{eff} curve, although the changes in the latter are relatively small. The temperature at which the event takes place on heating (103 °C) is in good agreement with the literature

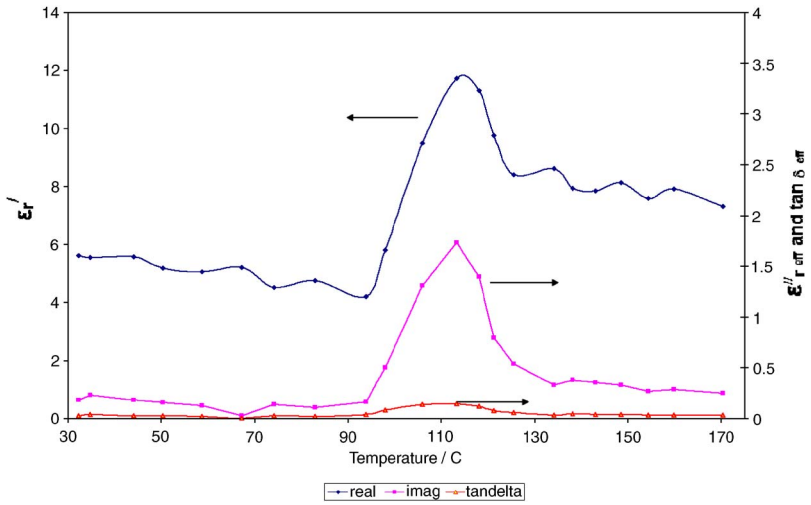

FIG. 6. (Color online) Variation of dielectric properties of zinc acetate with respect to temperature while heating.

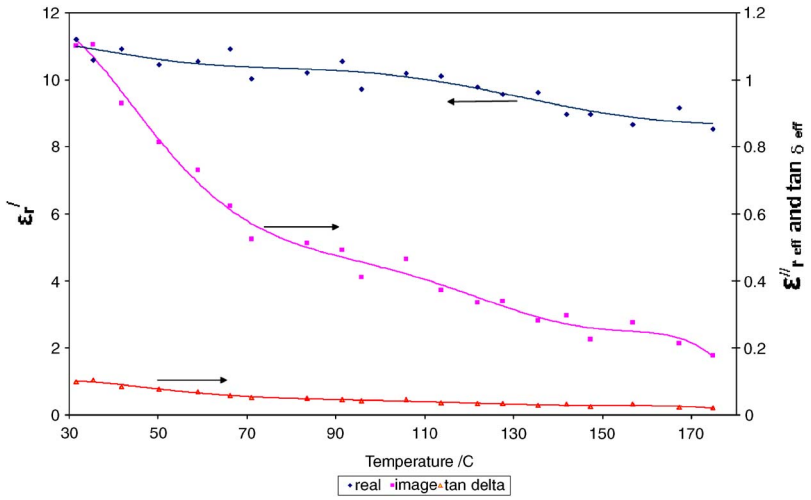

FIG. 7. (Color online) Variation of dielectric properties of zinc acetate with respect to temperature while cooling.

value of 106 °C found using conventional thermal analysis techniques. We attribute the rapid increase in ε_r' and $\varepsilon_{r\,\mathrm{eff}}''$ to the increased mobility of water of crystallization during the dehydration process. As the water was progressively lost from the surface the values are seen to reduce.

On cooling the sample, now in its dehydrated state (Fig. 7), no discontinuity was observed in the dielectric parameters, indicating that the dehydration was irreversible under the conditions used, as expected. It should be noted that, as this is a cooling experiment, this figure should be read from right to left, i.e., the experiment starts at the right hand side.

C. Melting

Melting is an important phenomenon both industrially and academically and stearic acid was used to illustrate the role of MDTA in investigating this type of process during microwave heating. The plot of the dielectric constant as a function of temperature (Fig. 8) showed a step as the sample underwent melting. However, the plot of $\varepsilon_{r\,\mathrm{eff}}''$ against temperature produced only a suggestion of a small peak at approximately 68 °C, while tan δ_{eff} exhibited only very small changes over the temperature range studied.

Figure 9, which should be read from right to left, shows the curves obtained while the sample was cooled. It shows that the solidification, which of course is reversible, unlike the dehydration of zinc acetate reported above, has the opposite effect on the dielectric parameters and that there is excellent agreement between the heating and cooling data. Both show a good correlation with the literature value for the melting point of 69 °C.

VIII. SUMMARY

The results presented in this article demonstrate the development of instrumentation which provides the scientific community with a new thermoanalytical technique (MDTA). This technique is unique in that it detects thermally induced transformations in materials via changes in their real and imaginary permittivities. The data presented confirm MDTA to be applicable to the study of both chemical and physical processes. Furthermore, it is applicable to thermally induced transformations in any type of solid sample, providing there is a change in the magnitude of either or both the real and imaginary permittivities. While MDTA is equally valid for materials with low and high values of ε' and ε'', the important feature that determines its sensitivity is the magnitude of their changes during the transformation being studied, rather than the absolute values.

Experimentation has shown that the MDTA technique benefits from the use of an inert sample diluent. While this is a long accepted methodology in thermal analysis that is

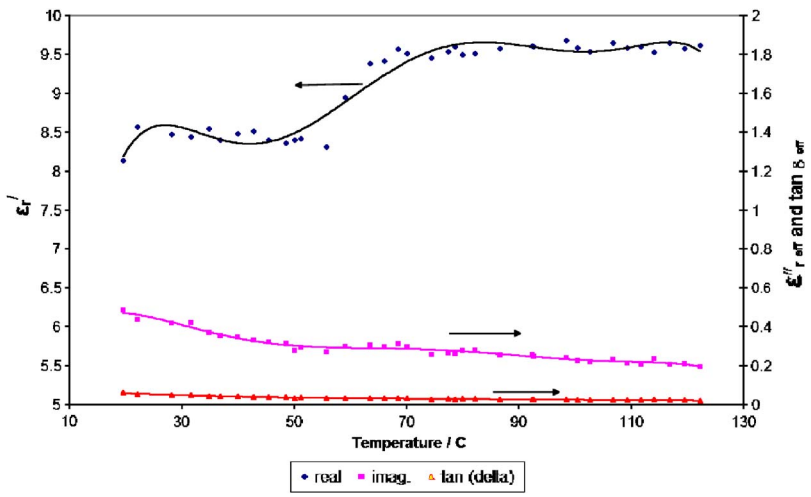

FIG. 8. (Color online) Variation of dielectric properties of stearic acid with respect to temperature while heating.

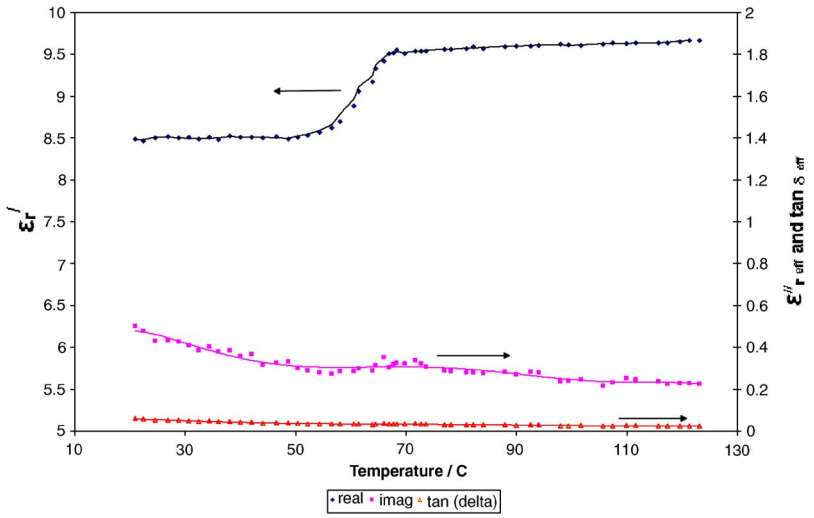

FIG. 9. (Color online) Variation of dielectric properties of stearic acid with respect to temperature while cooling.

known to confer many advantages, modern thermoanalytical instruments require very small samples and hence preclude this as a routine method. There is a drawback, however, to using sample dilution which is that ε' and ε'' all have values which are not far removed from those of the silicon carbide diluent. This is as may be expected and results simply because the analyte is only present at concentrations varying from 4.7 to 16.6 wt %. It is not seen as being particularly problematic as the primary aim of the work has not been to report absolute values for the dielectric constant of materials as a function of temperature but to demonstrate that, as noted above, MDTA can be used to detect thermally induced processes. While it is encouraging that the measured values of the dielectric constants of pure silicon carbide, both real and imaginary, are in reasonably close agreement with those reported in the literature, it is not of paramount importance in this instance. In terms of problems arising during materials processing using microwave heating, the key parameters are not usually the absolute values of the dielectric properties but the magnitude of their changes, as it is these that can lead to difficulties in temperature control. For these reasons, further validation of the precision of the values obtained was not deemed necessary at this stage.

However, when using pure materials, i.e., not diluted, our equipment is capable of measuring more accurate values for both the real and imaginary parts of the dielectric constant but, naturally, should experiments of this type be performed, further validation and calibration work would be needed to improve the precision.

MDTA relies on the use of relatively large samples to ensure good coupling with the microwave field. In certain circumstances this can be highly beneficial especially when obtaining a representative sample is difficult. Unfortunately, despite efforts to minimize temperature gradients within the sample, they are inevitable. This problem of temperature uniformity is not unique to MDTA. In conventional thermal analysis techniques, even when using very small samples, temperature gradients influence the width of the recorded event. In their infancy these techniques provided data which were far inferior to those produced by modern instruments. It is fully anticipated that the quality of the data available from MDTA will also increase as the technique develops and the instrumentation is refined.

While most instruments that have been developed to study the temperature dependence of dielectric properties employ conventional heating followed by rapid removal of the sample into the measurement cavity, MDTA uses *in situ* microwave heating. Microwave dielectric thermal analysis has been shown to be a powerful technique for revealing and studying thermal transformations. The results clearly show that measuring both the real and imaginary parts of the complex permittivity is essential in order to obtain the maximum information on a thermal transformation.

The behavior of materials within a microwave field prior to, during, and after thermally induced transformations is monitored. The variations of the complex permittivity with temperature will be of importance in industries and laboratories where microwave heating is used for the processing of materials.

Finally, as the instrument uses *in situ* measurement of the complex permittivity, it has the potential to provide information on the so-called "microwave effect" in which apparent deviations are found from the temperatures recorded using conventionally heated techniques such as differential scanning calorimetry (DSC) or differential thermal analysis (DTA). The results on AgI appear to be consistent with an apparent microwave anomaly, especially in view of the good agreement of our results with those of conventional techniques for the other two samples reported here. Although further work would be required to investigate this more fully, the equipment would seem to be eminently suitable for investigating this phenomenon.

The relative changes in the real and imaginary parts of the complex permittivity should be capable of yielding information regarding structural changes in materials. However, this is beyond the scope of this article.

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