**Temperature Dependence and Shape Effect in High-Temperature Microwave
Heating of Nickel Oxide Powders**

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20 **ABSTRACT**

21 The temperature dependence of microwave absorption was investigated for
22 NiO_x particles over the frequency range 2.0–13.5 GHz and temperature range
23 25–1000 °C. Using a coaxial transmission line method with a network analyzer, both
24 the real and imaginary parts of the relative permittivity (ϵ'_r and ϵ''_r , respectively) and
25 permeability (μ'_r and μ''_r , respectively) were measured; finding that both are largely
26 dependent on the temperature at all frequencies. Furthermore, permeability loss factors
27 related to shape effects were observed at high frequencies, indicating an increase in the
28 microwave-absorption properties. A modified form of Mie's theory was applied to
29 discuss these effects, wherein a spherical model demonstrating a close fit to the shape
30 effect data suggests a more complex microwave-absorption behavior at increased
31 temperature.

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35 1. INTRODUCTION

36 The use of microwaves (MW) has been extensively studied as an alternative means
37 of supplying energy in applications such as chemical reduction and heating [1-5]. For
38 example, Ishizaki and Nagata [2] constructed a high-power (120 kW), continuous
39 2.45-GHz MW furnace. Similarly, Peng *et al.* [3] constructed a 915-MHz, 225-kW MW
40 furnace to scale up steel production. In the field of organic chemistry, Verma *et al.* have
41 reported MW-enhanced reactions of ammonium molybdate with H₂O₂ that have
42 significant potential for the pretreatment of woody biomass by enzymatic
43 saccharification [4]. In addition, Yamaguchi *et al.* have demonstrated the successful
44 fabrication of face-centered cubic (fcc) Ni nanoparticles within an extremely short
45 duration by means of an MW-assisted intramolecular reduction of Ni²⁺ ions contained in
46 a formate complex with long-chain amine ligands [5]. In all these processes, the use of
47 MW irradiation provided excellent energy control, as well many advantages over
48 conventional methods, such as speed, product selectivity, and greater efficiency.

49 The use of MW heating for the synthesis of NiO_x has previously been
50 demonstrated by many researchers [5-8]. For instance, Lai *et al.* synthesized a
51 mixed-valence nickel oxide by precipitation from an aqueous solution of nickel nitrate
52 and sodium hydroxide, and by oxidation with sodium hypochlorite [6]; the time

53 required for phenol degradation being greatly reduced in either instance by MW
54 irradiation. Wang *et al.* also took advantage of MW irradiation in their synthesis of NiO_x
55 via the decomposition of basic nickel carbonate ($m\text{Ni}(\text{OH})_2.n\text{NiCO}_3.x\text{H}_2\text{O}$), because
56 NiO_x is a good absorber of MWs [7]. Once again, the use of MW heating enabled an
57 excellent control of the energy delivered to the processes and rapid production, with
58 Yoshikawa *et al.* also reporting a rapid carbothermic reduction of NiO_x [8]. In this, a
59 powdered mixture of NiO_x and graphite was heated by a single-mode MW applicator at
60 2.45 GHz, with the magnetic component of the MWs reported to enhance the reaction
61 rate. Consequently, processes employing NiO_x-MW combinations as a basic system for
62 the fabrication of catalytic agents have shown great benefits in terms of speed and
63 efficiency.

64 Despite all this, the temperature dependence of the MW-absorption properties of
65 NiO_x particles requires further investigation to adequately establish the chemical
66 concepts for each process, because NiO_x powders of various particles shapes were
67 employed in obtaining more efficient reaction rates. In particular, the permittivity and
68 permeability of NiO_x particles at a given MW frequency (which define its
69 MW-absorption properties) are expected to be largely dependent on the temperature
70 given the measurements obtained from other materials [9-11]. Moreover, because the

71 MW-absorption properties of NiO_x particles greatly influences their thermal distribution
72 at a microscopic scale (which is known as selective heating), and because the chemical
73 reaction by MW heating induces the anomalous behavior, the permittivity and
74 permeability are important considerations for the design of chemical processes. The
75 effect of the particle shape also needs to be taken into account, with NiO_x expected to
76 behave similarly to semimetal particles at temperatures of around 1000 °C based on its
77 electrical conductivity ($\sigma = 263 \text{ S cm}^{-1}$). Furthermore, because metal particles heated by
78 polaritons at MW frequencies change their absorption properties in relation to their
79 shape, the absorption properties of NiO_x particles are often very different from those of
80 a single crystal, as reported by Rao *et al.* [12].

81 In the present study, the temperature dependence of the MW-absorption properties
82 of NiO_x (i.e., permittivity and permeability) is experimentally investigated at
83 frequencies within the range 2.0–13.5 GHz and temperatures between 25 and 1000 °C.
84 Because the energy transfer from MW to particles is largely dependent on their
85 electrical conductivity and shapes, the effect of particle shape is also explored by
86 comparing the experimentally obtained data with theoretical predictions based on Mie
87 theory.

88

89 2. EXPERIMENTAL PROCEDURE

90 For this study, a NiO_x powder comprising 6×10^{-1} - μm -diameter particles with a
91 relative density of 4.80 g cm^{-3} was used (Supplemental Data 1). The real and imaginary
92 parts of the relative permittivity (ϵ'_r and ϵ''_r , respectively) and permeability (μ'_r and μ''_r ,
93 respectively) were measured across the temperature range 25–1000 °C and the
94 MW-frequency range 2.0–13.5 GHz using a coaxial transmission line method with a
95 network analyzer (Agilent Technologies, N5230A), coaxial cables, and an APC7 coaxial
96 sample holder (Fig. 1).

97 During the measurement, the temperature was increased at a rate of 10 °C/min
98 using an electric resistance furnace, during which the transmission and reflection (S
99 parameters) of the irradiated MWs were measured approximately every 50 °C. The
100 network analyzer had an output power of ca. 1 mW, requiring approximately 2 s for
101 each measurement. The complex permittivity and permeability were calculated from the
102 S parameters using an algorithm of the Nicolson-Ross model [13-14]; air being used as
103 a reference for calibration.

104 When the coaxial sample holder is heated, its length is increased by thermal
105 expansion, thus affecting the accuracy of the measurement. These differences between
106 actual and measured permittivity were shown to be quite large at frequencies in the

107 region 7–13.5 GHz, and at high temperature. A difference of 10 GHz was therefore used
108 as a reference frequency to determine the length of the sample holder (See Fig. 2).

109 The true temperature of the NiO_x was estimated from preliminary experiments. In
110 these, the temperature was measured with a thermocouple attached to the outer wall of
111 the sample holder, as opposed to a thermocouple embedded in the sample. Furthermore,
112 the apparent and true temperatures were measured simultaneously during the heating
113 cycle of the pre-experiment by using thermocouples attached to the outer wall of the
114 holder and embedded in the sample to calibrate the temperature. The measured
115 temperatures, therefore, represent an apparent temperature, from which the true
116 temperature of the NiO_x was estimated.

117

118 **3. RESULTS AND DISCUSSION**

119 As shown in Figure 3, the relative complex permittivity (ϵ'_r and ϵ''_r) of a NiO_x
120 powder is largely dependent on the sample temperature at frequencies 2.45–12.5 GHz,
121 with ϵ''_r increasing with temperature at all frequencies due to the fact that ceramics are
122 highly conductive at high temperature [12]. Furthermore, if it is assumed that the
123 permittivity of the NiO_x powder is $\epsilon_r \approx (\sigma/\omega)i$ (where σ is the static electrical
124 conductivity and ω is angular frequency), then the fact that electrical conductivity

125 increases exponentially means that ε_r will exhibit a similar behavior; which is typical
126 for the MW absorption of metal oxides [9,15].

127 The relative complex permittivity (ε'_r and ε''_r) of NiO_x , however, exhibits a very
128 different behavior to that observed with other powdered ceramics materials (magnetite
129 and hematite) at high temperature using a coaxial transmission line method [9,15].
130 Specifically, the relative complex permittivity of magnetite powders increases with the
131 temperature up to 600 °C, but decreases beyond this point. Hematite powders exhibit
132 the same tendency, albeit with a critical temperature of 700 °C. In contrast, the relative
133 complex permittivity of NiO_x does not decrease; instead, it remains constant at 700 °C.
134 However, considering that these previous studies did not correct for the thermal
135 expansion of the coaxial sample holder during heating, it is considered that the present
136 results are a more accurate reflection of the true behavior. Furthermore, given that the
137 that the relative complex permittivity (ε'_r and ε''_r) of NiO_x exhibits a similar tendency as
138 this uncorrected previous work, it is reasonable to assume that this correction is
139 effective in removing the measurement noise.

140 Figure 4 shows the temperature dependence of the relative complex permeability (μ'_r
141 and μ''_r); we can see that at low frequencies, NiO_x maintains a constant value, but
142 exhibits strong absorptions at 10 and 12.5 GHz. To determine whether this absorption

143 phenomena is at all related to the shape of the particles, the frequency dependence of the
144 permeability loss needs to be taken into consideration.

145 The influence of particle shape on MW absorption at different frequencies was
146 predicted by Mie theory, with the effects of spherically shaped particles being
147 determined theoretically [16-17]. Ignatenko *et al.* have previously reported that when
148 considering the energy loss of these materials in a MW field, it is not possible to ignore
149 the effect of the magnetic component and still achieve a good correlation between the
150 analytical solution and experimental results [18-19]. Assuming that their theory and
151 experimental results are indeed correct, it is the combined effect of the magnetic field
152 and high temperature that influences the electrical conductivity and particle radius of
153 NiO_x powders, and thus, determines the overall shape effect.

154 Figure 5 shows the frequency dependence of the loss factor estimated from the
155 relative complex permeability (μ'_r and μ''_r), which shows that at frequencies 2–7 GHz,
156 the loss factor is reduced with increasing temperature. This tendency is easily
157 understood if we consider that the Neel temperature (T_N) of NiO is 252 °C. According
158 to Tanaka *et al.*, the heating of a magnetic field occurs due to the response of
159 magnetization to MWs, which originates from electron spins residing in unfilled 3d
160 shells. The resulting non-resonant response causes a large change in the internal energy

161 through exchange interactions between spins, which is larger than the Zeeman term.
162 Each electron spin is, therefore, able to respond to the alternating magnetic field of the
163 incident MWs, even above T_N . This energy change is, in turn, dissipated to the lattice
164 and contributes to heating [20]. It should be noted here that although Tanaka *et al.*
165 employed the Heisenberg model to describe the Curie temperature, the difference
166 between the Neel and Curie temperatures does not change the form of the model.
167 Considering this, it is reasonable to assume that the loss factor decreases with increasing
168 temperature at frequencies in the range 2–7 GHz.

169 At frequencies in the range 7–13.5 GHz, the loss factor increases with temperature
170 due to the particle shape effect. Figure 6 shows the simulated results of MW absorption
171 per volume based on the assumption that all of the NiO_x particles were perfectly
172 spherical [21]; the application of the analytical methods used to describe the shape
173 effect have been reported by Ignatenko *et al.* [16]. This theory is based on a
174 modification of Mie's theory, and does describe the shape effects quite well. As such,
175 these calculations show that the absorption properties of the magnetic field increase as
176 the electrical conductivity of the NiO_x particles increases. Thus, the absorption of NiO_x
177 is at a maximum when σ is almost equal to 1.0 S m^{-1} , but then decreases with any
178 further increase in electrical conductivity. The absorption at high frequency exhibits a

179 similar tendency, with the simulation indicating that the observed absorption properties
180 are consistent with Mie's theory.

181 The electrical conductivity of NiO_x increases exponentially with decreasing
182 $(-\frac{E_\sigma}{kT})$, and is proportional to σ_0 ; where σ_0 is the frequency factor, k is the Boltzmann
183 constant, and E_σ is the activation energy. The σ_0 and E_σ values have been reported by
184 Mitoff *et al.* for single NiO crystals within the high temperature range 560–1155 °C; the
185 electrical conductivities have been calculated using these values [22]. Employing this
186 data, a formula relating the electrical conductivity and temperature was obtained, the
187 absorption properties calculated by this being then compared against the experimental
188 data.

189 Figure 7 is indicative of the comparison between the simulated temperature
190 dependence of MW absorption per volume and the observed magnetic field loss factors
191 for a frequency of 11.1 GHz. This reveals that both the theoretical and experimental
192 results indicate a maximum absorption at a given temperature. In this particular instance,
193 the theory predicts a shape effect at a temperature of 6.25×100 °C; whereas in reality,
194 resonance was observed at 6.37×100 °C. Considering the variation in particle size and
195 thermal distribution of actual particles, this theory clearly incorporates this shape effect
196 phenomenon quite well.

197

198 **4. CONCLUSIONS**

199 The temperature dependence of the MW-absorption properties of NiO_x
200 particles was investigated within the frequency range 2.0–13.5 GHz. From this, the real
201 and imaginary parts of the relative permittivity (ϵ'_r and ϵ''_r , respectively) and
202 permeability (μ'_r and μ''_r , respectively) were measured over the temperature range
203 25–1000 °C using a coaxial transmission line method with a network analyzer to
204 establish the chemical concepts for each process. The relative complex permittivity of
205 NiO_x particles was found to be largely dependent on the temperature at all frequencies,
206 and ϵ''_r increased with temperature. The permeability of NiO_x exhibits strong absorption
207 at 10 and 12.5 GHz, a region in which the loss factor increases with temperature due to
208 particle shape effects. This result is well described by Mie theory, wherein the loss
209 factor indicates complex behavior with changes in temperature. Within the frequency
210 range 2–7 GHz, the loss factor decreases with increasing temperature, which is
211 attributable to a loss of magnetism caused by exceeding the Neel temperature.

212

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276 [21] Supporting Information: The shapes of NiOx particles were investigated in this
277 study. Through SEM imaging, the particles were found to all be the same size, which
278 indicates a low aspect ratio (Supplemental Data 2). Therefore, an analytical model based
279 on a sphere was employed in this study.

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283

284

285 **FIGURE CAPTIONS**

286 **FIG. 1** Experimental setup used for measuring relative permittivity. An R-type
287 thermocouple is attached to the 300-mm-long SUS316L stainless steel sample holder by
288 Pt wire. The apparent temperature (T_{app}) varies almost linearly with the true temperature
289 (T_{true}) according to $T_{\text{app}} = T_{\text{true}} \times 1.0313 + 43.237$, which was used to correct the
290 temperature for all data.

291

292 **FIG. 2** Real part of permittivity for air, as calculated using the Nicolson-Ross
293 model. In the absence of NiO_x inside the sample holder, the permittivity should be 1.
294 Assuming that thermal expansion lengthens the sample holder, the change of length can
295 therefore be estimated to maintain the accuracy of the measurement according to $L = 1.6$
296 $\times 10^{-3} T + 300.83$; where L is the estimated length at temperature T .

297

298 **FIG. 3** Temperature dependence of the relative complex permittivity (ϵ'_r and ϵ''_r)
299 for NiO_x powder (particle size: $6 \times 10^{-1} \mu\text{m}$; relative density: 4.80 g cm^{-3}) at frequencies
300 of (a) 2.45, (b) 5, (c) 7.5, (d) 10, and (e) 12.5 GHz. At all frequencies, ϵ'_r and ϵ''_r
301 increased with temperature. The loss factors are higher at lower frequencies ($=\epsilon'_r/\epsilon''_r$).

302

303 **FIG. 4** Temperature dependence of the relative complex permeability (μ'_r and μ''_r)
304 for NiO_x powder (particle size: 6×10^{-1} μm ; relative density: 4.80 g cm^{-3}) at frequencies
305 of (a) 2.45, (b) 5, (c) 7.5, (d) 10, and (e) 12.5 GHz. The results for NiO_x were constant
306 at all frequencies, except for 12.5 GHz.

307

308 **FIG. 5** Frequency dependence of the loss factor estimated from the relative
309 complex permeability (μ'_r and μ''_r) at 25, 297, 491, 685, and 830 °C. A moving average
310 method was utilized for noise removal (average rate: 3.7%). The absorption properties
311 at low frequency decrease with increasing temperature, whereas those at high frequency
312 increase with the magnetic field.

313

314 **FIG. 6** Frequency dependence of MW absorption per volume, as simulated using a
315 spherical model. Maximum absorption for NiO_x occurs at frequencies in the range
316 7.5–12.5 GHz, which were determined by the electrical conductivity and radii of the
317 sphere.

318

319 **FIG. 7** Simulated temperature dependence of MW absorption per volume, and
320 observed magnetic field loss factors at a frequency of 11.1 GHz; where $E_\sigma = 0.66 \text{ eV}$ and

321 $\sigma_{\text{NiO}} = 3.0 \times 10^3 \Omega \text{ cm}^{-1}$. Both theoretical and experimental data indicate a maximum
322 absorption at the same resonance temperature, which is qualitatively predicted by the
323 Mie theory.
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Fig. 4 Suagawara et al.

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Fig. 6 Sugawara et al.

Fig. 7 Suagawara et al.

Supprimenntal Data 1: Sugawara et al

Supplemental Data 2: Sugawara et al.