

COMPONENT PART NOTICE

THIS PAPER IS A COMPONENT PART OF THE FOLLOWING COMPILATION REPORT:

TITLE: Ceramic Transactions. Volume 21. Proceedings of the Symposium on  
Microwave Theory and Application in Materials Processing Annual  
Meeting of the American Ceramic Society (23rd) Held in Cincinnati, OH  
on April 29-May 3, 1991.

TO ORDER THE COMPLETE COMPILATION REPORT, USE AD-A253 631.

THE COMPONENT PART IS PROVIDED HERE TO ALLOW USERS ACCESS TO INDIVIDUALLY AUTHORED SECTIONS OF PROCEEDING, ANNUALS, SYMPOSIA, ETC. HOWEVER, THE COMPONENT SHOULD BE CONSIDERED WITHIN THE CONTEXT OF THE OVERALL COMPILATION REPORT AND NOT AS A STAND-ALONE TECHNICAL REPORT.

THE FOLLOWING COMPONENT PART NUMBERS COMPRISE THE COMPILATION REPORT:

AD# AD-P007 716 thru AD# P007 783  
AD# \_\_\_\_\_ AD# \_\_\_\_\_  
AD# \_\_\_\_\_ AD# \_\_\_\_\_

**DTIC**  
**ELECTE**  
**S B D**  
**AUG 13 1992**

DTIC QUALITY INSPECTED 8

**DISTRIBUTION STATEMENT A**  
Approved for public release  
Distribution Unlimited

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

AD-P007 720



## FUNDAMENTAL INTERACTION MECHANISMS BETWEEN MICROWAVES AND MATTER

R.E. Newnham, S.J. Jang, Ming Xu, and Frederick Jones

Materials Research Laboratory  
The Pennsylvania State University  
University Park, PA 16802

### ABSTRACT

A molecular and crystallographic view of the absorption of microwave energy by ceramic materials is presented, with examples drawn from both structural and electronic ceramics, together with the liquid and polymeric materials used in processing them. Among the absorption mechanisms discussed are dipole reorientation, space charge phenomena, ferrimagnetic resonance, and tails from the far infrared. Other important topics include relaxation spectra, field partitioning, and thermal runaway.

### INTRODUCTION

Many different physical phenomena are involved in the microwave processing of ceramics. Microwaves are electromagnetic waves ranging from 1m to 1mm in wavelength at frequencies from 0.3 to 300 GHz. The interaction with matter takes place through the electric field vector  $E(V/m)$  and the magnetic field vector  $H(A/m)$  belonging to the microwave. The purpose of this paper is to review the fundamental interaction mechanisms between microwaves and matter.

### ELECTRIC LOSS

When subjected to an electric field, materials polarize creating an electric polarization  $P(C/m^2)$  equal to the dipole moment  $(C \cdot m)$  per unit volume  $(m^{-3})$ .

There are four important polarization mechanisms in solids, and three of them lead to losses in the microwave region: (1) space charges arising from localized electrical conduction, (2) rotating electric dipoles, and (3) ionic polarization associated with far-infrared vibrations.

In discussing these phenomena, it is helpful to describe the losses in terms of the real and the imaginary parts of the dielectric constant  $K^*$ . The electric field of the microwave is given by

$$E = E_0 e^{i\omega t} \quad (1)$$

92-20578



where  $E_0$  is the amplitude of the field,  $\omega$  is the angular frequency,  $t$  the time, and  $i = \sqrt{-1}$ . The resulting electric flux density is

$$D = D_0 e^{i(\omega t - \delta)} \quad (2)$$

where  $\delta$  is the phase angle associated with the time lag in polarizing the material. The electric flux density (electric displacement) comes from the applied electric field and the electric polarization:

$$D = \epsilon_0 E + P = \epsilon E \quad (3)$$

where  $\epsilon_0 (= 8.85 \times 10^{-12} \text{ F/m})$  is the permittivity of free space, and the dielectric constant is the relative permittivity of the material

$$K^* = \frac{\epsilon}{\epsilon_0} = \frac{D}{\epsilon_0 E} = \frac{D_0 e^{-i\delta}}{\epsilon_0 E} = K' - iK'' \quad (4)$$

The real part of the dielectric constant is in phase with the field

$$K' = \frac{D_0 \cos \delta}{\epsilon_0 E} \quad (5)$$

and the imaginary part is out of phase

$$K'' = \frac{D_0 \sin \delta}{\epsilon_0 E} \quad (6)$$

The loss factor  $\tan \delta$  is  $K''/K'$ .

As pointed out by Sutton (1989), the power absorbed per unit volume is

$$W = \frac{1}{2} E_0^2 \omega \epsilon_0 K'' = \frac{1}{2} E_0^2 \omega \epsilon_0 K' \tan \delta \quad (7)$$

Microwave absorption therefore increases with field intensity, frequency, loss factor and dielectric constant. It is also important to realize, however, that in microwave processing we are dealing with inhomogeneous materials. Generally there are ceramic particles, organic vehicles, and porosity present in the green ceramic body. In this case we must be aware that electric fields are also inhomogeneous (Meek, 1987). Flux continuity ( $D_1 = D_2$ ) is required across

interfaces if both phases are insulators. This means that electric fields are largest in regions of small permittivity.

## CONDUCTION LOSSES

Most ceramics are wide band gap semiconductors with resistances that decrease rapidly with temperature. Sintered alumina is an excellent high voltage insulator with resistivity in excess of  $10^{14} \Omega\text{-m}$  at room temperature, but it drops to less than  $10^{10} \Omega\text{-m}$  at  $400^\circ\text{C}$  and  $10^5 \Omega\text{-m}$  at  $1000^\circ\text{C}$ . Other ceramic insulators such as steatite and porcelain decrease even faster. At  $400^\circ\text{C}$  the resistivity of steatite is about  $10^8 \Omega\text{-m}$ , and porcelain with its mobile alkali ions is only about  $10^4 \Omega\text{-m}$ .

Metallic behavior is observed in some transition metallic oxides. Rhenium trioxide ( $\text{ReO}_3$ ) is comparable to silver and gold with resistivity less than  $10^{-8} \Omega\text{-m}$  at room temperature.  $\text{RuO}_2$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{PdO}$ , and tungsten bronzes such as  $\text{Na}_{0.8}\text{WO}_3$  are also excellent conductors.

The importance of conduction losses in microwave heating is borne out in the experiments of Walkiewicz, Kazonich and McGill (1988). In this study a wide variety of metal powders, inorganic chemicals, and mineral specimens were heated in a microwave oven and the temperatures recorded as a function of time. The results are summarized in Table 1.

Table 1. Microwave heated minerals, chemicals, and metal powders. Temperatures were recorded after a few minutes heating at power levels near 1kW. (McGill, et al, 1988) approximate resistivities are given in parentheses.

<u>Metal powders</u> ( $10^{-6} - 10^{-8} \Omega\text{-m}$ ) Al, Co, Cu, Fe, Mg, Mo Moderate heating to about $400^\circ\text{C}$	<u>Oxide minerals</u> ( $10^4 - 10^{14} \Omega\text{-m}$ ) $\text{SiO}_2$ , $\text{Al}_2\text{O}_3$ , $\text{KAlSi}_3\text{O}_8$ , $\text{CaCO}_3$ Very little heating only about $80^\circ\text{C}$ .
<u>Alkali Halides</u> ( $10^4 - 10^5 \Omega\text{-m}$ ) KCl, KBr, NaCl, NaBr, LiCl Very little heating. Only about $50^\circ\text{C}$ .	<u>Sulfide semiconductors</u> ( $10^{-3} - 10^{-5} \Omega\text{-m}$ ) $\text{FeS}_2$ , PbS, $\text{CuFeS}_2$ Easily heated to about $1000^\circ\text{C}$ .
<u>Mixed Valent Oxides</u> ( $10^{-2} - 10^{-4} \Omega\text{-m}$ ) $\text{Fe}_3\text{O}_4$ , CuO, $\text{Co}_2\text{O}_3$ , NiO Easily heated to about $1000^\circ\text{C}$	<u>Carbon and Graphite</u> ( $\sim 10 \Omega\text{-m}$ ) Easily heated to $1000^\circ\text{C}$ .

It is apparent from these observations that conduction promotes the coupling of microwave energy into the powder. Transition metal oxides and sulfides such as magnetite and pyrite are easily heated, but insulators like alumina and silica are not.

Note, however, that metal particles are not heated as well, despite their high electrical conductivity.

Metals do not heat as well as semimetals and narrow-band semiconductors because electric fields cannot penetrate much below the surface. Skin depth,  $\delta$ , is defined as the depth at which the electric field drops to  $1/e = 0.368$  of the surface value. It is related to frequency  $f$ , permeability  $\mu$  and conductivity  $\sigma$  by the relation

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} \quad (8)$$

For copper,  $\sigma = 5.8 \times 10^7 \Omega^{-1}m^{-1}$ ,  $\mu \equiv \mu_0$ , where  $\mu_0$  is the permeability of free space, and the skin depth is approximately 1 cm at 60 Hz and less than  $1 \mu m$  at microwave frequencies. Since field penetration is proportional to  $\sigma^{-1/2}$ , microwave energy heats semimetals and semiconductors better than copper. Note also that the resistance of metals increases with temperature, unlike that of semiconductors which show a rapid decrease. This promotes rapid heating and thermal runaway for the latter, as explained later.

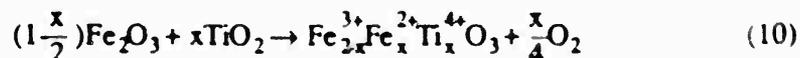
The inhomogeneous nature of green ceramics can be understood using the Maxwell-Wagner model (von Hippel, 1954). For a two-layer system consisting of equal amounts of conducting high-permittivity material (e.g., ferrite) and an insulating low-permittivity material (air or polymer), the relaxation frequency at which absorption occurs is

$$\omega = \sigma/\epsilon. \quad (9)$$

This lies in the microwave region when the resistivity  $\rho$ , expressed in  $\Omega \cdot m$ , is about  $10/K$ , where  $K$  is the dielectric constant. Hence, semiconductors and semimetals have about the optimum conductivity for ceramic processing at microwave frequencies.

## OXIDE SEMICONDUCTORS

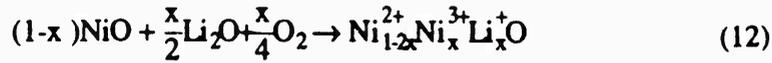
Transition metal oxides like magnetite with mixed cation valences are among the best microwave absorbers with very rapid thermal runaway. In electroceramic technology these mixed valency oxides are used as NTCR (negative temperature coefficient of resistance) thermistors. The electrical resistance decreases exponentially with increasing temperature. Typical of the NTCR thermistor materials, also known as controlled valency semiconductors, are titanium-doped hematite ( $Fe_2O_3:Ti$ ) and lithium-doped bunsenite ( $NiO:Li$ ). Reacting hematite with rutile in air yields



This is an n-type semiconductor in which electrons are transferred between iron atoms of different valence



p-type NTC thermistors are made from nickel oxide doped with lithium.



The hole conduction process involves charge transfer between trivalent and divalent nickel ions.



Doped nickel oxide has the rocksalt structure with lithium partially replacing nickel in the cation sites. Ionic radii for  $\text{Ni}^{2+}$  (0.84Å),  $\text{Ni}^{3+}$  (0.74Å), and  $\text{Li}^+$  (0.88Å) all favor octahedral coordination with oxygen.

The resistivity of  $\text{Ni}_{1-x}\text{Li}_x\text{O}$  ceramics decreases drastically with increasing lithium content. The resistivity at  $x=10^{-4}$  is about 1000 Ωm and at  $x=0.1$  it drops to 0.01 Ωm. The color is another indication of increased conductivity. The green color of pure nickel oxide deepens to black with increased doping.

For semiconducting compositions near  $\text{Ni}_{0.95}\text{Li}_{0.05}\text{O}$ , the band gap is about 0.15eV. The physical origin of this narrow band gap is attributed to the weak attractive forces between the negatively charged portion of the lattice where  $\text{Li}^+$  dopant ions are located, and positively charged regions occupied by the compensating  $\text{Ni}^{3+}$  ions. Charge is neutralized best when these ions are next, nearest neighbors, but under the action of electric field or temperature, the electron hole located at the  $\text{Ni}^{3+}$  drifts away rather easily to other nickel sites. Polarization of the surrounding oxide lattice also contributes to the band gap energy.

Electrical conductivity  $\sigma$  is proportional to the charge carrier concentration  $n$ , the charge of each carrier  $q$ , and the mobility  $\mu$ :

$$\sigma = n q \mu \quad (14)$$

In thermistors and other materials subject to thermal runaway, the temperature dependence of the conductivity is of great importance. Both  $n$  and  $\mu$  are strongly dependent on temperature. For a semiconductor, the carrier concentration varies exponentially with temperature

$$n \sim \exp(-E/kT) \quad (15)$$

where  $E$  is the energy required to liberate charge carriers,  $k$  is Boltzmann's constant and  $T$  is the absolute temperature. The temperature dependence of the mobility depends on its physical origin. For most scattering processes, mobility follows an inverse power law

$$\mu \sim T^{-b} \quad (16)$$

in which mobility decreases with increasing temperature because of atomic thermal vibrations, but a different temperature dependence is observed for hopping processes. Here the mobility depends on thermal excitation, and increases exponentially with temperature

$$\mu \sim \exp(E'/kT). \quad (17)$$

$E'$  is the energy observed in the hopping process. Summing up, the temperature dependence of the electrical conductivity is

$$\sigma(T) \sim T^{-b} e^{-(E+E')/kT} \quad (18)$$

Since exponentials tend to dominate, the electrical resistance of a mixed valency oxide can be described by

$$R = Ae^{B/T}. \quad (19)$$

For the transition metal oxides used as NTC thermistors,  $R$  lies in the range  $1-10^4$  ohms, and  $B$  is  $2000 - 6000^\circ\text{K}$ . The temperature coefficient  $\alpha$  describes the fractional change in resistance with increasing temperature:

$$\alpha = \frac{1}{R} \frac{dR}{dT} = \frac{B}{T^2} \quad (20)$$

At room temperature, the resistance drops by  $2-6\%/^\circ\text{K}$  for a typical thermistor. Resistance changes typical for thermistors made from transition metal oxides are shown in Fig. 1

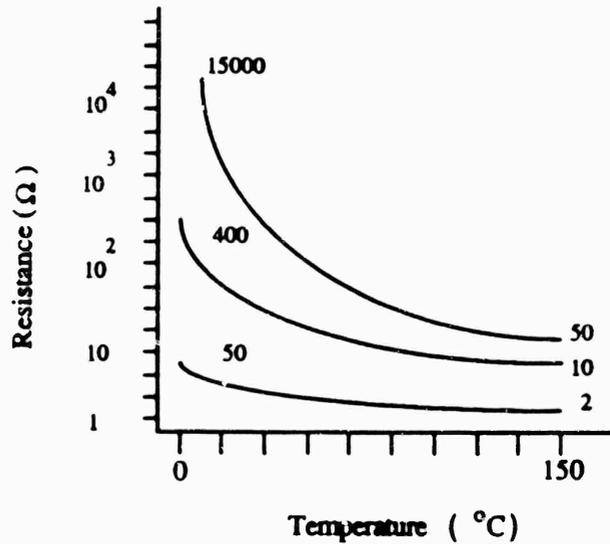


Fig. 1. Temperature dependence of typical NTC thermistors.

#### THERMAL RUNAWAY

A typical current-voltage relationship for a transition metal oxide thermistor is shown in Fig. 2. This is a so-called static characteristic in which the current is set to constant value and the system is equilibrated. The steady state voltage and temperature are then recorded for each current setting. Runaway takes place if the current is not carefully controlled.

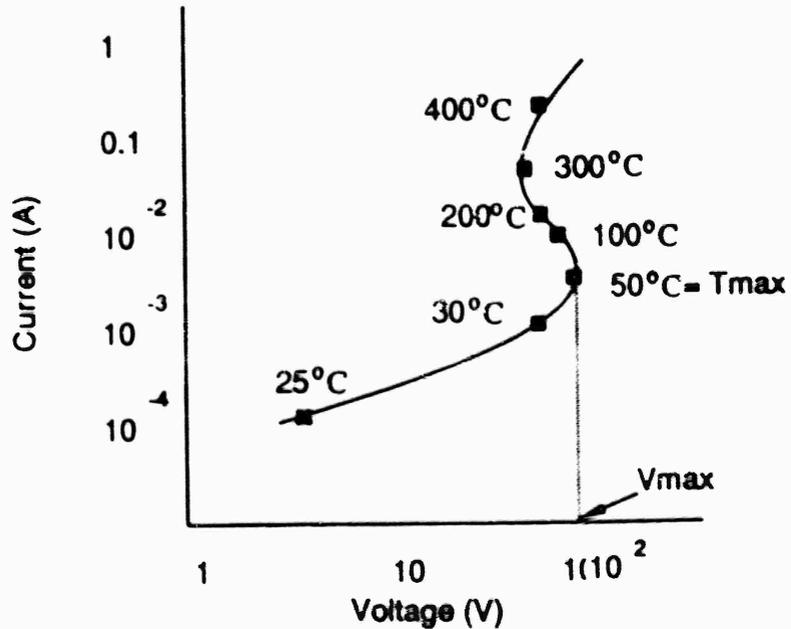


Fig. 2. Current-voltage characteristic for a transition metal oxide thermistor. Runaway takes place above T<sub>MAX</sub> and V<sub>MAX</sub>.

The relationship between the I-V characteristic (Fig. 2) and the R-T relationship (Fig. 1) is established by through Ohm's Law and the power balance equation:

$$R = V/I = Ae^{B/T} \quad (21)$$

$$W = VI = AD(T-T_0). \quad (22)$$

W is the input power (watts), T the specimen temperature, T<sub>0</sub> the temperature of ambient, and D the coefficient in Newton's law of cooling. D is a measure of the thermal coupling to the surroundings per unit surface area of the specimen. When surrounded by air, the specimen is cooled by convective air currents, and D ranges from 5 W/m<sup>2</sup>K for free convection to 50 W/m<sup>2</sup>K for forced convection (Tummala). The values of D are substantially higher, typically 100 - 10,000 W/m<sup>2</sup>K, when in thermal contact to the surroundings takes place through solids or liquids.

Converting Ohm's law and the power balance equation to logarithmic form and summing the two, we obtain an expression relating voltage and temperature:

$$2\ln V = \ln AD + \ln (T-T_0) + B/T. \quad (23)$$

Thermal runaway takes place when T exceeds T<sub>MAX</sub> and V exceeds V<sub>MAX</sub>. To determine these conditions, we take the derivative of the voltage-temperature relation at T = T<sub>MAX</sub>, V = V<sub>MAX</sub> and

$$2 \frac{d}{dT} \ln V = 0 = \frac{1}{T_{MAX} - T_0} - \frac{B}{T_{MAX}^2} \quad (24)$$

$$T_{MAX} = \frac{B}{2} \pm \sqrt{\frac{B^2}{4} - BT_0} \quad (25)$$

For B = 2000 - 4000 K, and T<sub>0</sub> = 30°C, T<sub>MAX</sub> is in the range 45-85°C, which is not far above room temperature. Therefore many transition metal oxides are on the verge of thermal runaway, as evidenced by the microwave heating experiments. The corresponding values for input current and power are obtained from the equation balancing input and output power using the appropriate value for D.

#### MICROWAVE ABSORPTION IN SILICATES

Conduction losses are important in glasses as well. Fused silica has very low tan δ values (<0.001) over wide frequency and temperature ranges. Alkali ions promote dielectric loss in glass. At low frequencies the loss is associated with ion transport through the silicate network giving a space charge contribution to the

dielectric permittivity. At 1 MHz the dielectric constant of sodium silicate glasses containing 30 mol% Na<sub>2</sub>O. 70 mol% SiO<sub>2</sub> are about twice as large as SiO<sub>2</sub> glass.

Vibration losses become important at higher frequencies. Localized motion of the alkali ion in silicate cages can lead to strong absorption in the microwave range. The undesirable heating of Corning 9609 glass-ceramic cooking ware is an excellent example (MacDowell, 1984). Sodium nepheline (Na<sub>4</sub>Al<sub>4</sub>Si<sub>4</sub>O<sub>16</sub>) is the crystalline phase in this ceramic whose microwave losses are far higher than those of natural nepheline (KNa<sub>3</sub>Al<sub>4</sub>Si<sub>4</sub>O<sub>16</sub>). The glass-ceramic has a tan  $\delta$  of about 7% at 2.45 GHz compared to 1% for the mineral nepheline. The high loss is attributed to the "rattling" motion of the smaller Na<sup>+</sup> ion occupying the crystallographic site of the larger K<sup>+</sup> ion. Sodium nepheline dishes are unsuitable for use in microwave ovens because of the high heat-up rate. The rattling motion of alkali ions can be pictured as localized conduction, or as a reorientable dipole between the cation and the coordinating anion cage. In this respect it bears a similarity to the double potential model used to describe proton motion in ice and ferroelectric potassium dihydrogen phosphate.

In most glasses, the tan  $\delta$  values continue to climb with higher frequency. These losses are especially prominent in lead-bearing glasses and can be thought of as tails from far infrared spectra. The atomic motion associated with these losses involve motions of heavy ions, or in some cases loosely bonded fragments of the silicate network, against the more tightly bonded portions of the network.

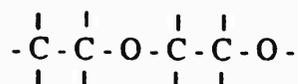
#### TAILS FROM THE FAR INFRARED

Most people have watched the ghostly "Tales from the Crypt," but few have given much thought to tails from the far infrared. They, too, are rather cryptic in that their origin is very obscure.

In crystals, infrared resonances involve the interaction of electromagnetic waves and the electric dipoles associated with lattice vibrations. The "reststrahlen" in alkali halides come from the excitation of a mode in which alkali ions vibrate out of phase with halogens. The frequency of this peak moves toward the far infrared and microwave region for heavy ions like Cs<sup>+</sup> and I<sup>-</sup>. Weaker bonding and heavier masses both contribute to the frequency shift. This idea is utilized in choosing infrared windows for optical systems.

Similar relationships are observed in polymer and composite systems. Vibrational motions in polymers involve large numbers of atoms (and hence large masses) and weak secondary bonding forces between polymer chains. The dielectric properties of polymers at microwave frequencies have been reviewed by A.J. Bur (1985). High frequency dielectric losses arise from various portions of the polymer structure. These include pendulum-like motions of bulky side groups, crankshaft motions of the main chain, "freezing-in" motions accompanying the rubber to glass transformations, and oscillations of the tiny crystallites present in semicrystalline polymers. Generally speaking, the smaller segments of polymer chains resonate at higher frequencies and are the last to be frozen out at low temperatures.

Poly (ethylene oxide) or PEO is a typical crystalline polymer with a melting point of 60°C and T<sub>g</sub> near -67°C. The helical chain has a backbone of carbon and oxygen atoms:



PEO has a modest dielectric constant of 4.3 at room temperature but a large absorption factor ( $\tan \delta \sim 0.1$ ) in the GHz range. Microbrownian motions of the main chain has been suggested as the cause of this absorption peak. Like glycerine, this peak is strongly dependent on temperature and frequency. At -50°C, the loss peak in PEO has dropped six orders of magnitude to the kilohertz range. (Connor, et al., 1964).

In amorphous polymers it is often difficult to identify the origin of microwave losses. Low density polyethylene (CH<sub>2</sub>)<sub>n</sub> has twice the microwave loss level of high density polyethylene. (Amrhein, 1972). The  $\tan \delta$  values increase slowly with frequency similar to the behavior of the high Q resonator ceramics. The higher losses of low density polyethylene have been attributed to the amorphous regions where portions of polymer chains are able to oscillate in response to the microwave field.

#### DIPOLE REORIENTATION

The loss spectrum of water illustrates the contributions of conductivity and dipole reorientation to the dielectric constant. Fig. shows the classical relaxation spectrum at room temperature. Water molecules have large dipole moments because of their nonlinear molecular geometry. Under an electric field the dipoles reorient easily at room temperature producing a large dielectric constant of nearly 80. At microwave frequencies there is a rapid decrease in the dielectric constant accompanied by a large loss peak which is utilized in cooking foods. The presence of water in meat and vegetables couples the microwave energy into the food. At lower frequencies there is additional loss arising from conduction. The temperature dependence of the dielectric properties at 3GHz and 1MHz are quite different. The microwave loss peak moves to higher frequencies with increasing temperature causing the 3GHz loss to decrease. On the other hand the 1 MHz loss increases with temperature as the water becomes more conducting. It is interesting to note that the dipole reorientation effects in water persist below the freezing point. The dielectric constant of ice is almost as high as water but the relaxation frequency drops rapidly into the kilohertz range and no longer couples strongly to microwaves.

Other polar liquids behave in a manner similar to water. Table 2 lists the microwave properties of several polar and non-polar liquids. Both the real and the imaginary parts of the dielectric constant of polar liquids are orders of magnitude larger than nonpolar liquids. Dipole reorientation is one of the dominant absorption mechanisms in the microwave region.

Many organic liquids show strong dispersion effects. Glycerol ( $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$ ) is a highly viscous polar liquid with a boiling point of  $290^\circ\text{C}$  and a melting point of  $18^\circ\text{C}$ . Dielectric spectra taken over a wide range of temperatures resemble the curious frequency - dependent curves of lead magnesium niobate (PMN) and other relaxor ferroelectrics. The broad, diffuse melting transition is accompanied by peaks in  $K'$  and  $K''$  which depend strongly on both temperature and measuring frequency. When measured at 100 Hz,  $K''$  peaks at  $-60^\circ\text{C}$ , and then shifts rapidly to higher temperatures for higher frequencies. At 10 kHz the peak is at  $-40^\circ\text{C}$  at 10 MHz,  $0^\circ\text{C}$ , and at 100 MHz,  $25^\circ\text{C}$ . Thus the absorption maximum in glycerol moves rapidly toward the microwave region as the temperature rises (Morgan and Yager, 1940).

It is this "tunability" of energy absorption that makes microwave processing especially interesting. Unlike normal furnaces with broad band heat sources, monochromatic sources such as microwave ovens and high power lasers offer the possibility of shifting the heating from one constituent to another as reaction and densification take place. Exploitation of this time-temperature-frequency feature seems likely.

Table 2. Microwave dielectric properties of liquids at 3 GHz and  $25^\circ\text{C}$  (vonHippel, 1954)

	$K$	$\tan \delta$
<u>Polar Liquids</u>		
Water ( $\text{H}_2\text{O}$ )	77	0.16
Methyl Alcohol ( $\text{CH}_3\text{OH}$ )	24	0.64
Ethyl Alcohol ( $\text{CH}_3\text{CH}_2\text{OH}$ )	6.5	0.25
<u>Nonpolar Liquids</u>		
Heptane ( $\text{CH}_3(\text{CH}_2)_5\text{CH}_3$ )	2.0	0.0001
Carbon Tetrachloride ( $\text{CCl}_4$ )	2.0	0.0004

#### MICROWAVE RESONANCE SPECTRA

Piezoelectric resonances also give rise to loss spectra, sometimes at very high frequencies. For thickness resonance, the fundamental frequency  $f$  is

$$f = \frac{1}{2t} \sqrt{\frac{c}{\rho}} \quad (\text{Hz}) \quad (26)$$

where  $c$  is the stiffness (approximately  $10^{11} \text{ N/m}^2$  for an oxide),  $\rho$  the density ( $\sim 5000 \text{ kg/m}^3$ ) and  $t$  refers to the specimen thickness in meters. Millimeter thick transducers have resonant frequencies in the MHz range, and extrapolating these results to the microwave range, it is apparent that micron-size piezoelectric particles will resonate at GHz frequencies. Ceramic grain sizes and ferroelectric domain sizes are in the micron range and therefore show electromechanical losses in the

microwave range. Experiments on  $\text{LiNbO}_3$  crystals, bicrystals and ceramics confirm these ideas (Yao Xi thesis).

The microwave losses in  $\text{BaTiO}_3$  are shown in Fig.3. Note the drastic reduction in loss in specimens placed under DC bias. With domain walls locked in position there is a large decrease in K.

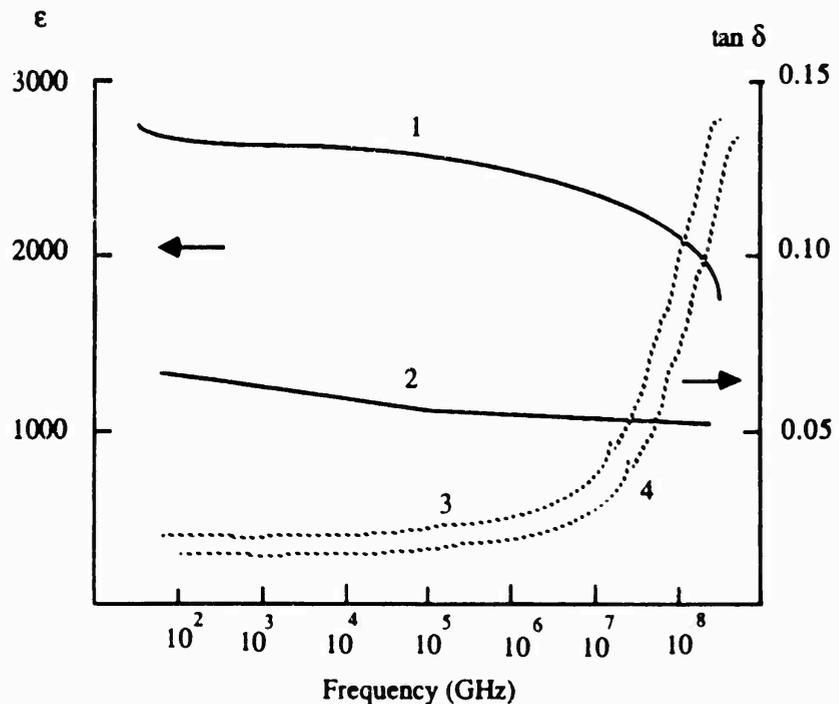


Fig. 3. Frequency dependence of the parameters of a poly-domain barium titanate crystal in weak fields. 1) Permittivity; 2) permittivity in a bias field of 10 kV/cm; 3) loss-angle tangent; 4) loss-angle tangent in a bias field of 10 kV/cm.

Fig. 3 Dielectric permittivity and loss tangent of  $\text{Ba}(\text{Ti}_{0.85}\text{Zr}_{0.11}\text{Sn}_{0.04})\text{O}_3$  ceramics change rapidly in the microwave region. Poling the ceramics inhibit domain wall motion and lowers both K and  $\text{Tan } \delta$ . (Poplavko, 1964).

Dimensional resonances of a different sort are employed in the dielectric resonators used in cellular mobile radios, marine satellite communications, and microstripline filters for SHF-TV converters. Dielectric resonance involves electromagnetic waves rather than the acoustic waves utilized in piezoelectric devices. The resonant frequency is controlled by the dielectric constant  $K (= \epsilon/\epsilon_0)$  and relative magnetic permeability  $\mu_R = \mu/\mu_0$ .

$$f = \frac{c}{\lambda \sqrt{K \mu_R}} \quad (27)$$

where  $c$  is the speed of light in vacuum and  $\lambda$  the wavelength. Resonance occurs when the specimen size corresponds to an integral number of wavelengths. High  $K$  dielectrics reduce the wavelengths and miniaturize the microwave filters.

The microwave loss spectra of typical dielectric resonators are shown in Fig. 4. Note that high  $K$  ceramics have higher losses than do low  $K$  materials, and that the losses generally increase at higher frequencies suggesting that the origin of these losses is in the far infrared.  $\tan \delta$  values for dielectric resonators are very small, typically  $10^{-3}$  to  $10^{-4}$ , and are probably associated with low frequency tails of far infrared absorption peaks.

The lowest frequency infrared mode involves vibrations of the large cation against the oxygen octahedra (Fig.5). The mode softens in high permittivity ferroelectric perovskites and eventually condenses at the Curie temperature to give spontaneous polarization. This helps to explain why high  $K$  dielectrics are generally more absorbing than Low  $K$  solids in the microwave region. The infrared peaks of dielectric resonator materials have been investigated by Wakino (1986).

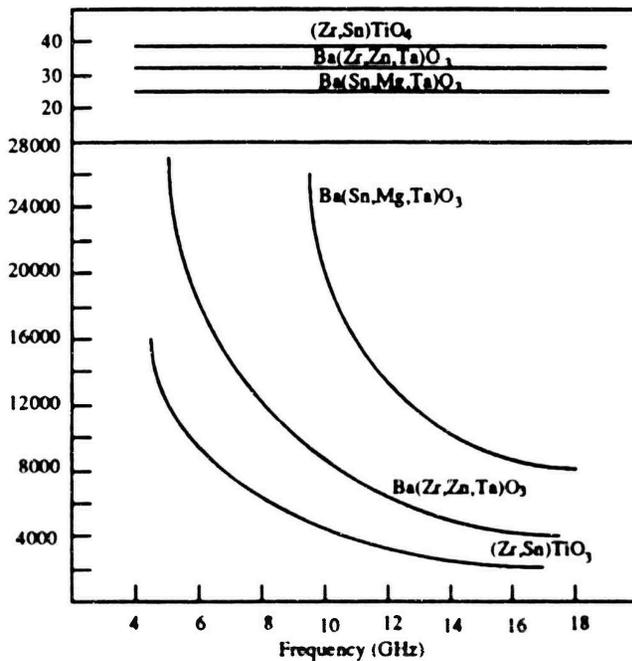


Fig.4. Microwave dielectric constants and loss spectra for ceramics used as dielectric resonators (Wakino, 1986).

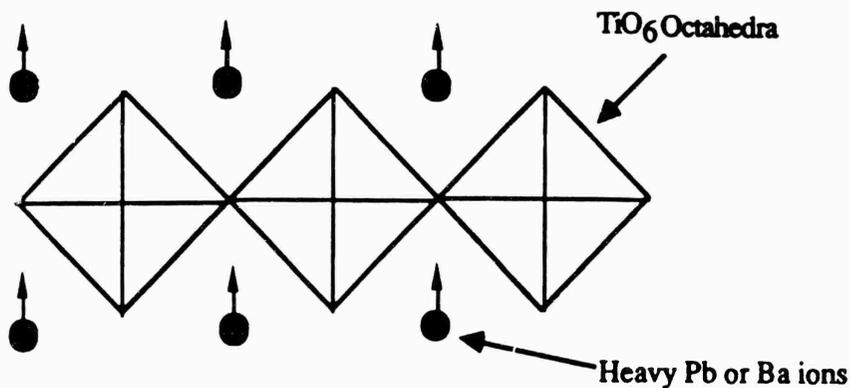


Fig. 5. Far infrared vibration mode for oxide perovskites. The vibrational mode of heavy ions of Pb or Ba, and  $\text{TiO}_6$  octahedra in the oxide perovskites.

### MAGNETIC LOSS

Most of the interactions between microwaves and matter take place through the electric vector of the electromagnetic wave, but the magnetic field vector can also induce substantial microwave losses, especially in magnetic materials with aligned spins. Some of the loss mechanisms in magnetic materials are listed in Table 3.

Table 3. Loss mechanisms in magnetic solids (Chikazumi, 1964)

Hysteresis loss rising from irreversible domain wall displacements

Eddy current loss from field-induced electric currents

Magnetic aftereffects associated with electron diffusion, usually from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$

Dimensional resonances coming from electromagnetic standing waves

Magnetic resonance from precessional motion of unpaired dipole magnetic moments

Domain wall oscillations

The magnetic field vector of the microwave is represented by

$$H = H_0 e^{i\omega t} \quad (28)$$

The resulting magnetic flux density is

$$B = B_0 e^{i(\omega t - \delta)} = \mu_0 H + I \quad (29)$$

where  $\mu_0$  is the permeability of free space ( $4\pi \times 10^{-7}$  H/m) and  $I$  is the magnetization (magnetic dipole moment per unit volume).

The magnetic permeability  $\mu$  is analogous to the electric permittivity  $\epsilon$ .

$$\mu = \frac{B}{H} = \frac{B_0 e^{-i\delta}}{H_0} = \mu' - i\mu'' \quad (30)$$

and the magnetic loss factor

$$\tan \delta_m = \frac{\mu''}{\mu'} \quad (31)$$

The relative permeability  $\mu_R = \mu/\mu_0$  is the magnetic equivalent of the dielectric constant.

The magnetic permeability of ferrites is strongly dependent on frequency. The resulting losses arise from conduction, ferrimagnetic resonance, and domain wall oscillations.

In magnetic ceramics, much of the microwave loss is associated with ferrimagnetic resonance which is observed in ferrites with the spinel, magnetoplumbite and garnet structures. As illustrated in Fig.6, ferrimagnetic resonance involves precessional motions of the sublattice magnetization vectors about an effective internal magnetic field  $H_e$ . The effective field is caused by domain wall resonance or by magnetocrystalline anisotropy. High frequency absorption in the microwave region is found in magnetic materials with large anisotropy coefficients  $K_1$ . Soft ferrites such as the manganese ferrites with the spinel structure generally show the highest loss in the MHz region whereas hard ferrites with the magnetoplumbite structure have much higher resonant frequencies up in the GHz range.

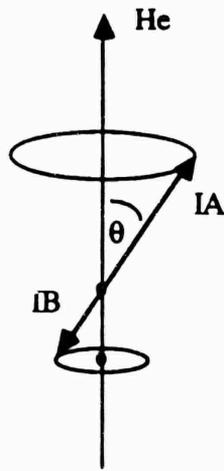


Fig. 6. Microwave resonance in ferrimagnetic oxides in which the sublattice magnetizations  $I_A$  and  $I_B$  precess about an internal effective field  $H_e$ .

### Summary

The interactions between microwaves and matter are many and various. Conduction losses from localized space charge effects are responsible for microwave loss in transition metal oxides with mixed valence states. The inhomogeneous nature of green ceramics can be modeled using Maxwell-Wagner theory and thermal runaway follows a process similar to that observed in NTC thermistors.

Alkali ions cause microwave loss in glasses and other silicates, especially when loosely coordinated in a manner allowing considerable rattling room. Oscillating Na ions can be pictured either as localized conduction or as reorientable dipoles. The two polarization mechanisms lose their identity in situations like this.

Organic compounds and polymers are useful in ceramic processing. Dipole relaxation spectra are common in water, alcohol and other polar liquids, leading to intense energy absorption in the microwave regions. Polymers also absorb in this region of the electromagnetic spectrum with smaller segments of the polymer chain resonating at higher frequencies and continuing to lower temperatures.

Localized resonances caused by piezoelectric electromechanical coupling can also cause microwave loss. Domains in ferroelectric ceramics are on the right size scale to promote loss in the GHz region.

Dielectric resonator materials such as  $ZrTiO_4$  utilize electromagnetic resonance rather than electromechanical resonance. These are generally low-loss ceramics but the  $\tan \delta$  values increase with frequency, suggesting a loss mechanism associated with infrared vibrations. Soft mode condensation in ferroelectrics has a similar origin.

Finally, not all microwave losses take place through the electric vector of the wave. The magnetic field vector can initiate energy transfer through magnetic resonance effects in which the unpaired electron spins precess about internal fields.

Anisotropy effects in hard ferrites and oscillating domain walls often create the internal fields.

### References

- E.M. Amhein, Ann. N.Y., " High Frequency Microwaves", Acad. Sci. 196 179 (1972).
- A.J. Bur, "Dielectric Properties of Polymers at Microwave Frequencies: A Review", Polymer 26 (7) 963-977 (1985).
- S. Chikazumi, Physics of Magnetism, Wiley, New York , (1964).
- T.M. Conner, et. al., " Microwave Loss in Polymers", J. Appl. Chem., 14, 74 (1964).
- Morgan and Yager, " Organic Dielectrics", Ind. Eng. Chem. 32, 1519 (1940).
- W.H. Sutton, Microwave Processing of Ceramic Materials. Ceram. Bull. 68 (2)376-386(1989).
- J.F. MacDowell, Microwave Heating of Nepheline Glass-Ceramics, Ceram. Bull. 63 (2) 282-286 (1984).
- S.L. McGill, J.W. Walkiewicz, and G.A. Smyres ,The Effects of Power Level on the Microwave Heating of Selected Chemicals and Minerals in Microwave Processing of Materials, Vol. 124. Mat. Res. Soc., Pittsburgh PA, 1988.
- T.T. Meek, Proposed Model for the Sintering of a Dielectric in a Microwave Field. J. of Mat. Sci. Lett. 6 638-640 (1987).
- Y.M. Poplavko, "Permittivity Dispersion of Barium Titanate Type Ferroelectric", Sov. Phy. - Solid State 6 [1] 45-49 (1964).
- R. Tummala and E. Rymazewski, Microelectronic Packaging Handbook, p. 171
- A.R. von Hippel (Ed.) Dielectric Materials and Applications M.I.T. Press, Cambridge, MA 1954.
- K. Wakino, "High Frequency Dielectrics and Their Applications", Proc. ISAF, 1986.
- Xi Yao, Dielectric and Piezoelectric Behavior of Lithium Niobate Bicrystals and Polycrystal Ceramics, Ph.D., Thesis, The Pennsylvania State University, (1982).