

Microwave Field Enhancement of Charge Transport in Sodium Chloride

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We describe the results of experiments designed to test for microwave enhancement of vacancy transport processes in NaCl. Experimental results indicate that intrinsic vacancy mobility is not enhanced by microwave fields. Instead, the evidence strongly suggests an enhancement of the driving force for charge transport. The experimental results display features consistent with a recent theory for microwave-enhanced driving forces in ionic conductors.

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A growing body of experimental data suggests that microwave heating of ceramic materials leads to enhanced diffusion or solid-state reaction rates when compared with conventional heating at the same temperature [1–7]. If microwave heating is perceived as a purely thermal process (by rapid equilibration of microwave energy to thermal energy of the material), then it is difficult to explain how microwave and conventional furnace heating can result in markedly different reaction rates. The several explanations attempted for these experimental observations fall into one of two classes: (1) nonequilibrium thermodynamics, and (2) “nonthermal” phenomena.

First, it has been argued that most temperature diagnostics only measure surface temperature and are therefore unreliable indicators of internal bulk temperatures. With microwave heating of low-loss materials, inverted temperature profiles (interior hotter than surface) occur at steady state as heat is lost from the surface, and it has been proposed that the internal temperatures responsible for the solid-state reactions exceed the measured surface temperatures by tens to hundreds of degrees Celsius. However, in some of the experiments referenced above (such as Ref. [3]), the sample dimensions and microwave absorption rates are both very small and therefore inconsistent with temperature differences of 50–200 °C between the surface and interior.

Several nonthermal hypotheses are based on the idea that microwave field disturbances of sufficient magnitude might enhance high-energy, nonthermal “tails” on ion energy or lattice phonon distributions [8,9]. Such effects would appear as an enhancement of ionic mobility or a lessening of the activation energy for ionic motion in such a lattice. However, calculations based on the phonon kinetic (Boltzmann) equation [10] indicate that these phenomena will be negligible for the microwave field intensities present in Refs. [1–7].

Most recently, Rybakov and Semenov [11] have proposed a model in which the microwave field induces near-surface oscillatory fluxes of ionic point defects that are rectified, yielding a net “ponderomotive” (time-averaged nonzero) transport of charged defects. In effect, the microwave field induces a nonequilibrium concentration of

vacancies in a small region near the surface of the ionic crystal. Mass flow is required to reach this nonequilibrium condition, and because the vacancies are charged, there is also an induced charge flow. If these nonlinear forces are large enough, they could explain the observations of microwave-enhanced diffusion reported in Refs. [3,6]. Whether they also explain enhanced densification rates during microwave sintering is still a matter of debate [12].

All of the microwave-enhanced processes studied in Refs. [1–7] can be characterized by a general relationship,

$$\text{RATE} = (\text{DRIVING FORCE}) \times (\text{TRANSPORT COEFFICIENT}). \quad (1)$$

For diffusion processes, the transport coefficient involves the carrier concentration c and the microscopic diffusion coefficient D , which for conditions near thermal equilibrium follows an Arrhenius-type behavior,

$$D = D_0 \exp(-Q/kT), \quad (2)$$

where Q is the activation energy for diffusion and kT is the thermal energy. Reports of enhanced process rates have so far been generally attributed to enhanced transport coefficients. Rybakov and Semenov (Ref. [11]) first explored the possibility that microwave fields could provide an additional driving force for charge flow.

We report here results comparing experimentally measured currents in sodium chloride (NaCl) crystals in the presence and in the absence of intense microwave fields. We interpret these currents to be ionic in nature. The ionic current (actually charge flux) through a ceramic sample induced by an applied bias voltage is

$$J_i = \frac{D_i c_i}{kT} z_i^2 e^2 \frac{V_{\text{bias}}}{\delta}, \quad (3)$$

where i refers to the most mobile charged species, J is the flux, c is the concentration, D is the diffusion coefficient, kT is the thermal energy, z is the valence, e is the electron charge, V_{bias} is the applied bias voltage, and δ is the crystal length. The ionic current depends on temperature, carrier concentration, carrier mobility (D), and applied voltage. Equation (3) assumes that the bias voltage is the sole driving force.

Our original intent was to test for nonthermal phenomena—that is, to determine whether microwave fields affected the crystalline lattice in such a way as to enhance the transport coefficient (i.e., increase D or c). We deliberately designed our experiments such that the microwave radiation would not appreciably raise the temperature of our sample; this precluded the possibility of inaccurate temperature measurement. If the temperature does not change during microwave irradiation, then both the carrier concentration c and the defect mobility D should remain constant. k , z , e , and δ are also constants in Eq. (3). The bias potential is an externally controlled variable. Hence, our original expectation was that an increase in the current during microwave irradiation would be directly attributable to an increase in D or c . Again, this was assuming that the bias voltage was the only driving force. The ponderomotive model (Ref. [11]) made us aware that the driving force may vary as microwave fields are applied.

To perform the ionic current measurements, an applicator was fashioned from a modified rectangular waveguide (Fig. 1). The applicator is heated conventionally using resistive heating tapes and maintained at a constant temperature. An external bias voltage pulse is applied across the ends of the crystal, and the resulting current is measured using a sensitive, high-gain amplifier. During the external bias pulse, microwave energy at 14 GHz is applied in 400 microsecond pulses—too short to heat the sample, but long enough to affect diffusion-time-scale events. The incident power is continuously adjustable between 0 and 2 kW, corresponding to microwave field intensities between 0 and 10^5 V/m. The use of conventional resistive heating combined with instantaneous *in situ* comparison of the microwave and microwave-free conditions has eliminated the concerns of inverted temperature gradients.

NaCl was chosen for these initial studies because it is a well-characterized ionic crystalline material. It has a simple defect chemistry (Schottky), it is available in high

purity or is easily doped, it has only one effective charge carrier (Na vacancies) in the extrinsic temperature range of these experiments, it has low microwave absorption, it is unaffected by most atmospheres, and it has a low melting temperature (800 °C). The last point is useful in that transport in refractory oxide ceramics can be emulated at much lower temperatures in NaCl.

Nominally pure (<10 ppm impurity concentration) NaCl single crystals were purchased from Harshaw-Bicron. The sample dimensions were 5 mm by 5 mm by 7.5 mm in length. Platinum electrodes were plasma sputter-deposited onto the ends of the samples.

With the NaCl sample situated in the experimental apparatus, we performed complex ac impedance measurements of the crystal (without microwave radiation) which confirmed two expectations. First, the resulting conductivities compared well with literature values [13,14] and so confirmed that we were measuring bulk ionic diffusion of sodium vacancies in the extrinsic regime. Second, it was found that an applied sinusoidal bias potential yields a sinusoidal ionic current from 10 Hz up to 1 MHz (the limit of the electronics). This linear response confirmed that the crystal is truly bipolar with no rectification properties at these frequencies. We are aware of no physical phenomena in NaCl, other than the ponderomotive model proposed in Ref. [11], that would provide rectification at GHz frequencies but not at MHz frequencies.

We also verified that the experimental system is not susceptible to anomalous electromagnetic or other electronic pickup. Microwave signals fed directly to the current measurement system fail to produce a detectable response. Measurements taken with no sample in the system display no enhanced current during microwave pulses, establishing that there are no “antenna pickup” or ground loop effects occurring in the experiments.

Having validated the capabilities of the experimental design, we proceeded to test for microwave radiation effects on ionic currents. In Fig. 2 we show the response of a NaCl crystal at 150 °C to both a bias voltage application and a pulse of microwave radiation. In Fig. 2(a) one observes the ionic current resulting from a bias application of 10 V. In the middle of this application, the microwave radiation is pulsed on and an increase in the current results. In Fig. 2(b) the applied bias voltage has been increased to 17 V, and the resulting ionic current has increased proportionately. Note, however, that the magnitude of the microwave-induced enhancement is essentially unchanged. This is clearly illustrated in Fig. 2(c) where we have applied no bias to the crystal, but a current still results from the microwave radiation. The magnitude of this microwave-induced current is virtually identical to the magnitude of the enhancements seen in Figs. 2(a) and 2(b). When a negative polarity bias is applied, the microwave-induced current retains the same magnitude and polarity as shown in Figs. 2(a)–2(c). The effect also retains the same magnitude when the crystal is

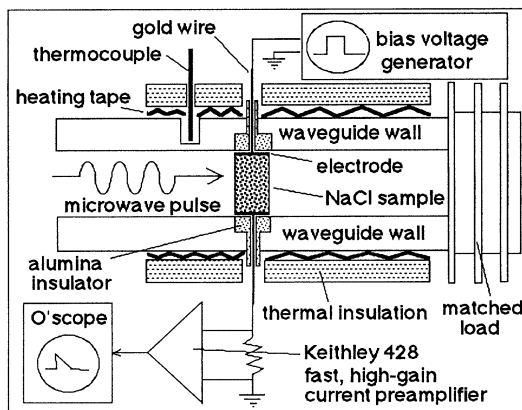


FIG. 1. Experimental configuration for measurement of ionic currents in NaCl.

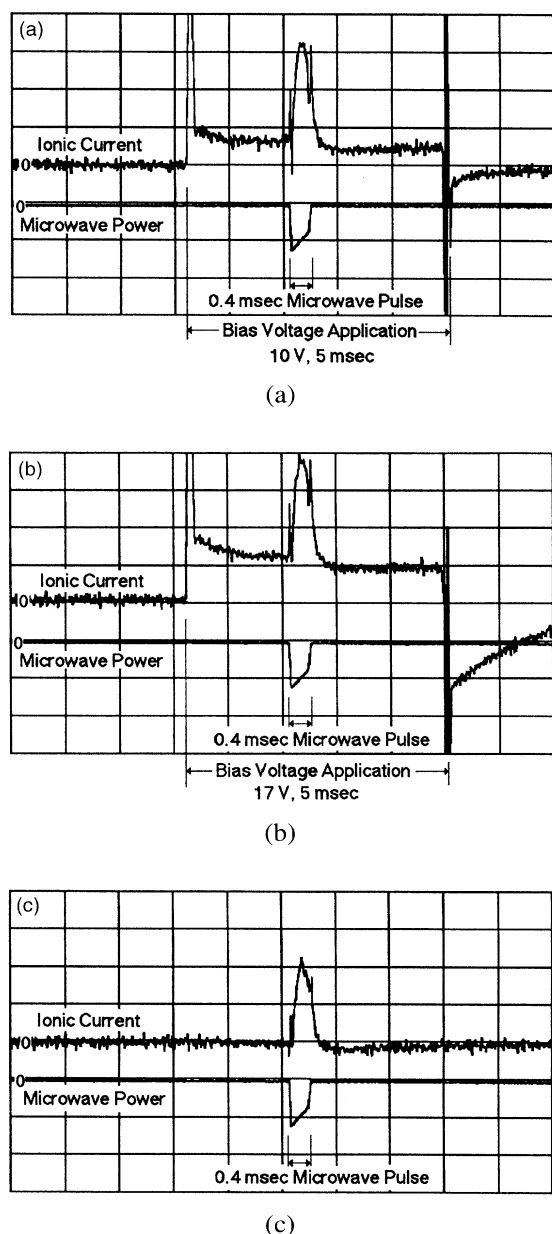


FIG. 2. Oscilloscope traces showing the effect of microwave irradiation on ionic currents in a NaCl crystal at 150 °C. In (a) an ionic current results from the application of a 10 V bias pulse and is enhanced during microwave irradiation (≈ 2 kW). In (b) the bias voltage is 17 V. In (c) we apply no bias voltage. In all three plots, the horizontal scale is 1 ms/div, and the vertical scale is 0.1 nA/div for the current.

removed and then reinserted. If the crystal is reinserted 180° with respect to its previous orientation, the polarity of the microwave-induced current changes.

The results shown in Fig. 2 are typical. Several crystals have been tested, and although the magnitude of the

microwave-induced current varies from sample to sample, the results are all within an order of magnitude. More importantly, the dependence of the effect on temperature and power remains the same from sample to sample. Figure 3 shows how the magnitude of the microwave-induced current varies with microwave power and temperature.

As seen by comparing Eqs. (1) and (3), the ionic current (flux) is the RATE, the voltage (times charge divided by crystal length) is the DRIVING FORCE, and the TRANSPORT COEFFICIENT, namely, the ionic conductivity, is determined by the concentration and mobility of vacancies. Thus we see between Figs. 2(a) and 2(b) that the ionic current resulting from the *applied bias voltage* has increased because the driving force has been increased from 10 to 17 V while the defect concentration and mobility have remained constant (same temperature). Consider now the current enhancement that occurs during microwave irradiation. If the mobility were increased and the driving force remained constant during irradiation, the magnitude of the enhancement would depend upon the applied bias voltage. This is clearly not the case. The data can only be explained by an enhancement of the driving force during microwave irradiation. This is most clearly exemplified in Fig. 2(c) where we have applied no bias and, hence, no obvious driving force. The current that results during the microwave pulse must therefore be *driven* by the application of microwave fields.

We considered the possibility that the microwave-induced current might be electronic in nature. Specifically, transition-metal ion defects in the crystal might act as semiconductor-type donors or acceptors. These electronic defects might then be rectified by the non-Ohmic semiconductor-to-metal junction at the electrode. It is difficult to explain, though, why such a rectification would not show up at 1 MHz or below. Further evidence against the possibility of semiconduction can be seen in Figs. 2(a)–2(c). Close examination shows that there is some relaxation of the current after the microwave pulse. The time constant of this relaxation closely matches that which follows the end of the applied bias pulse, and we

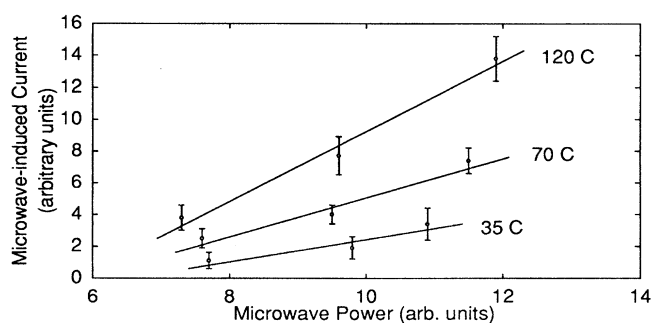


FIG. 3. Variation of microwave-induced current with microwave power and temperature.

have verified that the current during the applied bias is ionic. One would expect that electronic type defects would relax back to thermal equilibrium much faster than ionic defects. Note that careful experimentation has established that this relaxation is determined by the NaCl sample and is not a function of the external circuit.

Further, characterization of this phenomenon is so far consistent with the model put forth by Rybakov and Semenov, which predicts an effect that varies linearly with microwave power. Their model also shows the magnitude of the effect to depend on the defect concentration and mobility; it would thus increase with temperature, as does the ionic conductivity. The experimental results in Fig. 3 support these hypotheses.

As a final note, the experimental configuration as depicted *ideally* in Fig. 1 should not be able to detect the "ponderomotive" effect as described in Ref. [11]. The symmetry of the idealized configuration would result in microwave-induced currents at both electrodes that would cancel each other. In reality, however, obtaining a crystal with exactly identical end conditions is a practical impossibility, and this may account for why we measure a nonzero net current. Many potentially relevant factors (including surface roughness, electrode uniformity, and impurity concentrations at the end surfaces) and their effect on the measured currents are difficult to systematically control, prescribe, and quantify. The plasma sputter-deposition process used to deposit the platinum electrode seems so far to be the most important parameter. For example, a careful review of the precise steps taken during the sputter-deposition process reveals that there may be some limited, shallow platinum ion implantation. The first end of the crystal to be so coated may be receiving a slightly larger implanted ion concentration than the second side, resulting in a higher sodium vacancy concentration at that end. We believe that the process creates the asymmetry in the crystal's end surfaces that results in a net measurable result. This observation is consistent with a phenomenon (such as that of Ref. [11]) occurring in thin boundary layers ($\sim 100 \text{ \AA}$) at crystal surfaces.

In summary, a growing body of experimental data indicates that microwave processing of ceramic materials involves faster diffusion or solid-state reaction rates than conventional furnace heating. The questions of accurate temperature measurement, combined with the absence of a convincing theoretical explanation for the observations, has left the reports of microwave-enhanced diffusion and sintering rates subject to some doubt during the past eight years. In this article we have described results of experiments designed to measure the influence of microwave radiation on ionic currents in NaCl. The results are not subject to inaccurate temperature diagnostics and involve

in situ, instantaneous measurement of the response of charge transport in NaCl to microwave fields. The data suggest that intense microwave fields yield enhanced ionic currents in NaCl. This enhancement of charge transport is not the result of increased mobilities of defect species, but apparently involves an additional driving force. The data are consistent in several aspects with a recent model of high-frequency ponderomotive pressures exerted at the surface of ionic crystalline bodies.

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