Diffusion in Microwave-Heated Ceramics

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Microwave heating is an increasingly important method of chemical activation in both the laboratory and industrial processing. The increased breadth of microwave applications has not, however, been accompanied by a corresponding depth of understanding of microwave heating. The question of what constitutes a "microwave effect" remains unresolved, and that of whether "nonthermal" microwave activation takes place remains controversial. The effects of microwaves in solid materials and in biomolecules, in particular, are incompletely understood. In this paper, a method is described in which the effects of microwave heating may be investigated during the sintering of ceramic materials. By comparison of the diffusion rates parallel with, and perpendicular to, a polarized microwave field, the effects of thermal energy may be separated from those that are directly due to the microwaves. The results suggest that there is an enhanced sintering rate that is due to the presence of the microwave field, which becomes less significant as the sintering time increases. The results are consistent with a "ponderomotive" model that has been suggested previously and may have implications for reduced energy use in solid-state processing and for the rate at which thermally sensitive materials may be processed.

1. Introduction

Over the past 15 years, microwave dielectric heating has become an important method in chemical synthesis and materials processing.[1−4] In the solid phase, applications include single-phase sintering, reactive sintering of superconductors and magnetoresistors, preparation of oxides, nitrides and chalcogenides, the production of nanomaterials, ceramic joining, glassy phases, and the hydrothermal production of zeolites; some areas of which have been reviewed elsewhere.[5−8] Significant advantages, many of which stem from the unique nature of the energy transfer, have been observed in the microwave processing of ceramic materials. Microwave heating is characterized by several properties that make the technique fundamentally different from conventional heating methods and may lead to structural and chemical differences in the products, when compared to conventionally processed samples. In particular, microwave heating allows direct, volumetric, heating of the reaction components, with minimal requirements for energy to be expended in heating furnaces and containment materials. In small homogeneous samples, the heating can be effectively uniform throughout the sample, although perfect uniformity may be difficult to achieve in practice. In contrast with conventional heating, there is much less need for heat transfer

via thermal conduction within the sample, and this allows moderately large samples to be heated much more efficiently and with greater uniformity throughout the sample. The direct heating process also allows specific reactants to be heated, making it uniquely capable of generating extremely high temperatures in microscopic regions of the sample while maintaining lower temperatures in others.[9] This principle is most widely used in the specific heating of active sites in supported metal catalysts and has been applied, for example, in the rapid synthesis of metal chalcogenides from their elements.[10] Whatever may be the underlying cause, the practical result of these effects is that microwave-processed ceramics exhibit differences in density, porosity, grain size, thermal, and dielectric properties from those observed in conventionally processed samples. There are also advantages in the greater heating rates (of the order of around 100 K s^{-1}) that are possible with microwave heating. This has been used to generate 10^4-fold increases in densification rates of zinc oxide with concomitant suppression of grain growth.[11]

Many microwave-induced reactions in liquid phases that exhibited anomalous reaction rates have been satisfactorily explained in terms of effects such as superheating.[12] In the solid phase, however, a significant number of studies[13−16] still show that ion migration occurs due to a nonthermal

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mechanism. There is an expanding body of work on microwave-processed ceramic materials which describes enhanced mass transport and sintering rates corresponding to higher temperatures than those actually observed.[17-21] These results, and the unusual grain and pore morphologies resulting from microwave heating, have given rise to a claims for nonthermal effects as the primary cause. We here define "nonthermal effects" as those effects that result in the microwave electric field having a direct influence on ion motion, without the energy being first repartitioned into the various degrees of freedom in the solid.[22] Alumina has been a common material in comparative studies of microwave and conventional sintering. It has been almost invariably reported that sintering takes place at a lower measured temperature when microwaves are used by as much as 200 K.[23-25] Although careful measurements show the actual temperature reduction may be negligible, and certainly less than 50 °C,[26] claims that the effect is real, temperature and loss-factor independent, and cannot be attributed to temperature measurement errors[27] cannot be ignored. It has been noted that the improved sintering rate may be related to the increased lossiness in $Al_2O_3-ZrO_2$ composites with increased zirconia content rather than as a result of zirconia as a sintering aid.[28] It has also been noted that a lowering in the sintering temperature of alumina-based composites does not automatically increase with an increasing dielectric loss factor.[29] The lower temperatures and more rapid sintering rates that are associated with microwave heating increase the density of the final product but with a uniform pore and grain structure that persist until the final densification stages. Although there is a reduction on the sintering temperature, the final stages of densification are reported to result in similar grain sizes, irrespective of the heating method used.[30]

By study of the effect on alumina sintering of alumina-soluble aliovalent oxides such as MgO, it has also reported[31] that these have a significant reduction on the required sintering temperature which was mitigated on the addition of SiO_2. The addition of isovalent Sc_2O_3 additive in Al_2O_3, on the other hand, did not influence the sintering temperature, although concomitant distortion of the lattice is comparable to that from MgO solutes. This was suggested as an indicator

of the important role of point defects in the microwave sintering process. Dilatometer results on microwave-sintered $Al_2O_3-ZrO_2$ composites exhibited a microwave enhancement of the sintering process, suggested as stemming from a reduction in the activation energy for grain-boundary diffusion.[28]

The fundamental difficulty facing all such comparative work is that reliably determining the temperature of internal volumes in solids is not a trivial matter,[26] particularly if the material of interest displays poor thermal conductivity. In such cases, the scale and nature of thermal gradients between the heat source and the remaining volume of the sample cannot always be known. This problem is emphasized when microwave heating, a process characterized by direct volumetric energy transfer, is employed. Several factors contribute to the difficulty that the experimentalist faces. First, the energy is transferred directly, but not necessarily uniformly, into the sample. The volumes of maximal or minimal energy transfer may lie at a significant distance away from the point-(s) or area of temperature measurement. As the dielectric properties themselves are often heavily dependent upon the temperature, minor local temperature variations may become amplified through a positive feedback mechanism. It is therefore unreasonable to make the assumption that accurate temperatures in a microwave-heated system may be measured in a conventional manner. Where surface:volume ratios are small, optical methods do not give a reliable measure of internal temperatures, and the presence of thermocouples is known to perturb local fields and so significantly reduces their accuracy. Other methods, such as monitoring temperature-dependent lattice parameters, are not readily applied to inhomogeneous or imperfect systems. In many cases, although by no means all, results that were unequivocally attributed to nonthermal effects may be interpreted as a conventional consequence of inhomogeneous heating. While conventional heating may be assumed to give rise to uniform temperatures throughout a small sample, microwave heating imparts energy directly to the sample and, particularly within large samples, inhomogeneous heating may occur, although it has been calculated that significant thermal gradients may not be maintained across particles at the micron scale under steady-state conditions.[32]

In view of the practical difficulties associated with temperature measurement in these systems, it appears to be difficult to separate the direct effect of the electric field from the heat that the field may generate in a dielectric. If the electric field is directly responsible for nonthermal enhanced ion transport (whatever the precise mechanism), then an enhanced electric field should lead to an enhanced rate of the process in question. However, an increased electric field leads to greater heat generation and therefore enhanced rates of ion transport. Rather than rely on the strength of the electric field, this work investigates the effects of the *direction* of the electric field upon the rate of ion transport. A novel method is described, which has been used in a preliminary determination of the effect of the microwave field on the mass transport. The effect of the microwave field on

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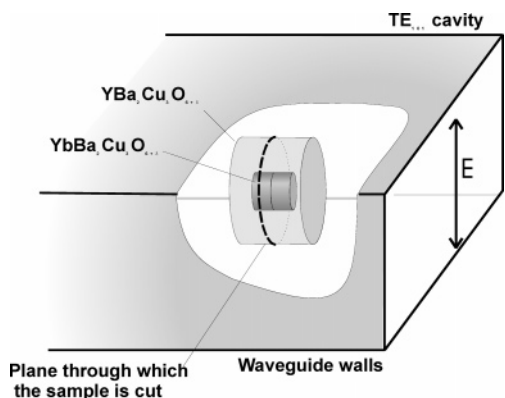
Figure 1. Schematic representation of the sample arrangement. The sample is held in the center of the cavity using a low-density, low-loss ceramic (not shown).

mass transport is experimentally investigated as a function of the angle to the microwave electric field rather than by comparing samples heated under different regimes.

2. Experimental Details

To investigate the question of whether mass transport is affected by the presence of a microwave field, it is desirable that the influence of temperature must be, as far as possible, removed from the experimental method. Whatever effects may be attributed to particular influences of the microwave field, it is reasonable to assume that the manifestation of the effect is increased by the presence of an increased microwave field. Difficulties arise because an increased microwave energy density will also result in an increased heating effect, thus making accurate temperature measurement necessary.

Evaluating the strength of microwave effects within a single, uniformly heated, sample circumvents the inherent difficulties arising from the comparison of conventionally heated and microwave-heated samples. An experimental arrangement has been employed that almost entirely circumvents the need to measure the sample temperature. This is possible because comparison is no longer made between two different samples where one is conventionally heated and one heated using microwaves. Instead, the comparison is made between diffusion parallel *with* the electric field vector and diffusion perpendicular *to* the microwave electric field vector.

A schematic diagram of the sample arrangement for this study is shown in Figure 1. A 3 mm diameter pellet of one material is embedded inside a larger (13 mm diameter) pellet of a second material. The two materials are selected to be isostructural, with chemical compositions that differ by at least one element. The sample materials were also selected for their relatively high dielectric loss tangents and hence a capacity to undergo microwave heating. A typical example is $YBa_2Cu_3O_{7-\delta}$ embedded in $YBa_2Cu_3O_{7-\delta}$. The selection of such pairs of materials allows the diffusion of, for example, Yb^{3+} ions into $YBa_2Cu_3O_{7-\delta}$ to be measured following microwave or conventional heating. The (Y/Yb)$Ba_2Cu_3O_{7-\delta}$ samples were synthesized by heating stoichiometric quantities of $(Y/Yb)_2O_3$, $BaCO_3$, and CuO using standard methods. In other studies, silver β''-alumina was synthesized from a commercial sample of sodium β''-alumina and silver nitrate, again using literature methods. Once prepared, the samples were analyzed by powder X-ray diffraction and ground to a fine powder using a ball mill before being sieved using a 50-μm sieve.

Following careful preparation, the sample is placed in a polarized microwave field, achieved by placing it centrally within a waveguide operating in the TE_{01} mode, and directly heated using 2.450-GHz

microwaves. In each case, the applicator was tuned so as to optimize energy transfer to the sample, as determined by minimization of the reflected power. Each sample was then processed at an elevated temperature for a period of between 2 and 12 days. As the experiment is designed to determine the rate of diffusion as a function of its angle to the field polarization, an extremely shallow longitudinal line was prescored along the outer surface of the sample. This was used to indicate the polarization of the applied microwave radiation during subsequent analyses. While temperature is not a critical variable in this work, a grounded thermocouple was briefly and periodically inserted to ensure that sample temperatures were sufficiently high for diffusion to take place at a measurable rate.

Conducting materials, such as those employed in this study, have a natural matching to (i.e., optimal energy transfer from) waves with low E/H ratios.[33] Under the conditions employed, the E/H ratio is simply a function of the position of the sample relative to those of the standing wave. The sample was therefore simply placed at the optimum position in the cavity for heating to take place. Although the E-field in the sample is low compared to the applied field, it is nonzero, and the efficiency of the coupling to the sample more than compensates for this. The electric field within the sample is partially derived from Faraday's law; $\nabla \times E = -(\partial B/\partial t)$. The sample was thus heated by microwaves from a continuously variable power source with an intensity sufficient to maintain a temperature of ca. 750 °C for (Y,Yb)$Ba_2Cu_3O_{6+\delta}$ samples and ca. 250 °C for (Na,Ag) β''-alumina samples. These temperatures were selected so that sufficient thermal energy was available to generate a measurable level of ion motion in preliminary trials.

After heating, the sample is cut in cross-section at precisely 90° to its major axis, and the exposed face polished to a fine finish using <1-μm diamond powder. The orientation of the sample is continuously and randomly varied during polishing, to prevent the introduction of systematic effects from the sample processing. The sample surface is then analyzed using X-ray fluorescence analysis on a scanning electron microscope (SEM). Throughout the process, the score mark indicating the direction of the microwave field polarization was retained, as knowledge of the direction of the field polarization within the sample is critical to the subsequent analysis. A rotating stage within the SEM allowed the surface to be sampled at any selected angle to the original field polarization. The contrast in the signal intensity of the SEM backscattered electrons allowed ready location of the interface between the two materials, which represents the region of interest. Once the interface was located, elemental mapping of the ion distributions along a radial line perpendicular to the interface was performed using X-ray fluorescence. At each point, a minimum number of three scans was obtained and the resulting information averaged.

The intensity of a particular line in the X-ray fluorescence spectrum is directly related to the amount of a specified element in the sampling region. The relative concentration of the elements may therefore be plotted as a function of radial distance across the interface (Figure 2).

While the cylindrical geometry used does not permit a rigorous analytical solution to Fick's diffusion laws, simplification of the analysis is permissible without the introduction of any significant errors. The diffusion layer is 3 orders of magnitude smaller than the sample, and the diffusion in any radial direction is therefore effectively indistinguishable from the one-dimensional case described in standard texts. It is therefore possible to calculate the diffusion coefficient, D, by fitting the measured concentration,

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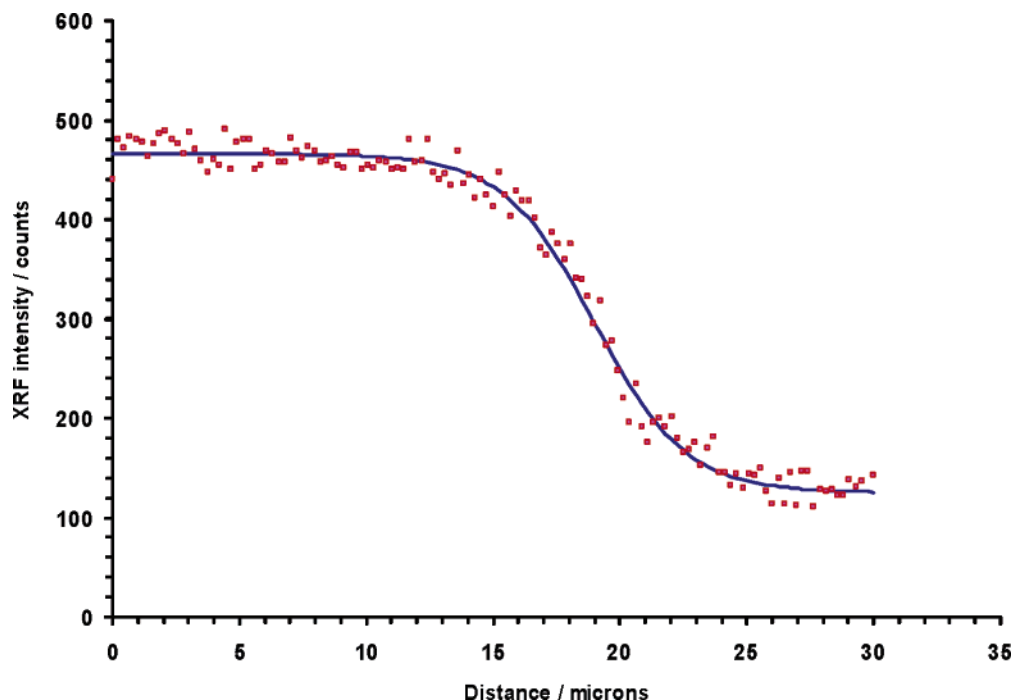
Figure 2. Typical concentration−distance plot (Y^{3+} diffusing into $YbBa_2Cu_3O_{6+\delta}$).

$C(x,t)$, at a position x, and after a time, t, to the expression

$$C(x,t) = \frac{C'}{2}\left[1 + erf\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

where C' is a constant and the standard error function, $erf(z)$, is given by the expression

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-x^2)\,dx$$

In practice, it proved simpler to fit to a more analytical expression

$$C(x,t) = C'(1 + \exp((c_x - c_0)/(Ax)))^{-1}$$

where A is a constant and c_x and c_0 are the relative concentrations at positions x and the center of the distribution, respectively. The parameters were then related back to the original formula, an *apparent* diffusion coefficient obtained, comprising the effects of conventional diffusion (whose value will be unchanged from that of an equivalent conventionally heated system) *and* that of a hypothesised additional driving force. By performing these measurements at a number of points around the pellet, it is possible to generate a polar plot showing the apparent diffusion coefficient as a function of angle to the microwave electric field vector. For each angle, a minimum of three concentration−distance plots were obtained and the mean relative diffusion coefficient calculated. Example plots are shown in Figure 3. The results from conventionally heated samples were also taken in order to determine whether the sample preparation method was responsible for any apparent anisotropy in the diffusion.

3. Results and Discussion

3.1. Spacial Dependence of the Diffusion Rate. The principal consideration of this work has been an analysis of the relative diffusion of ions as a function of the angle to the microwave field, and it was therefore important to establish the effect of the processing upon the results. Careful preparation of the sample is very important, as inadequate

polishing results in a distinctive pattern due to "smearing" of the phases over one another. Extended polishing regimes with the finest grit were introduced and used in all subsequent studies. In most cases, it proved possible to obtain a concentration−distance plot that could be correlated with very high goodness of fit to the theoretical diffusion function, although local structure problems, such as partial separation of the two compounds, prevented the analysis of some scans.

In the control studies, the relative diffusion coefficient was compared in a conventionally heated sample, in the absence of any deliberately introduced electric field. As expected, this results in isotropic diffusion as a function of angle to an arbitrary axis (Figure 3a), indicating that, as expected, there is no preferred direction for the diffusion of ions in the solid state. The plot is not, however, *perfectly* isotropic. Some variation can be seen in the angular dependence even in the conventionally heated sample. Clearly, this arises from the nonideal nature of the sample material, and may arise from, for example, variations in kinetic barriers when diffusion takes place from certain "more labile" crystal faces.

In contrast to the conventionally heated samples, the results from the samples that were subjected to polarized microwave irradiation show a distinctly different angular dependence than that observed from conventionally processed samples. In all cases, there is a preferred diffusion direction that is consistently found to occur parallel with the microwave electric field vector. The apparent diffusion coefficient parallel with the field is observed to be up to 10 times greater than that perpendicular to it under the conditions that were employed. Although there are margins of error in these results, the measurements are found to be reproducible between samples.

The sample material pairs that have been used for these measurements to date have been $YBa_2Cu_3O_{6+\delta}/YbBa_2$-$Cu_3O_{6+\delta}$ and Ag^+/Na^+ β'' alumina. In both cases, it has been found that the same "hourglass" plot is observed when the

(a)

(b)

(c)

(d)
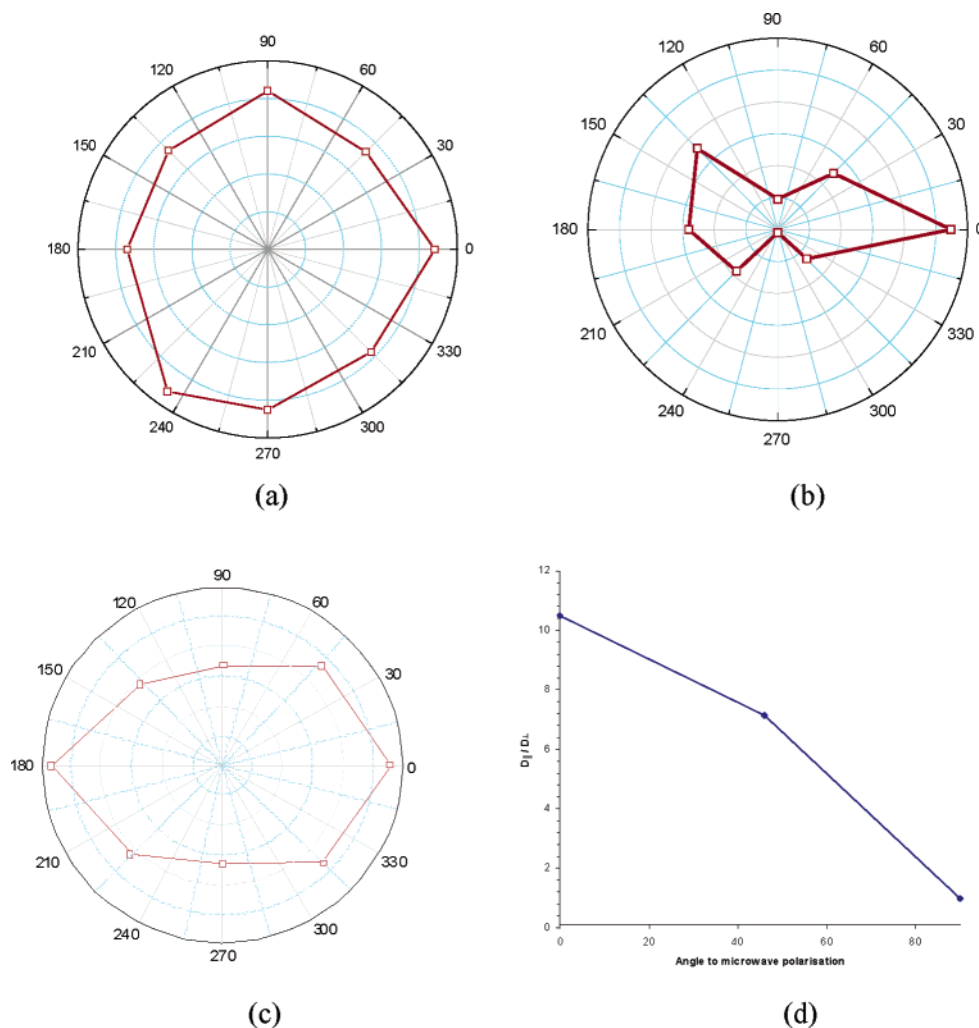
Figure 3. Polar plot of the relative diffusion coefficient (radial axis) for Y^{3+} diffusing into $YBa_2Cu_3O_{7-\delta}$ as a function of angle to the microwave polarization. The radial axis represents the apparent diffusion coefficient: (a) conventially heated sample, 10 days at 800 °C; (b) sample heated by microwaves polarized along the $0-180°$ axis, 5 days at ca. 700 °C; (c) sample heated by microwaves polarized along the $0-180°$ axis, 13 days at ca. 700 °C). (d) Alternative presentation of data in part b, allowing for symmetry in the sample.

diffusion coefficient is plotted as a function of angle to the microwave polarization, indicating that, whatever the origin of the effect, it is not specific to just one material. The results obtained for Y^{3+} as it diffused into a $YBa_2Cu_3O_{6+\delta}$ matrix are shown in parts b and c of Figure 3. As the electric field is alternating along a prescribed axis, it follows that the distribution of diffusion around the sample should be symmetrical about the two major axes, and this is indeed the case. Thus, within each 90° sector of the cross section, the diffusion has been measured at 0, 45, and 90° to the polarization axis, and it is possible to plot the mean relative diffusion coefficient as a function of these angles. In this form, the relation of the relative diffusion coefficient to the polarization angle is more clearly seen to fall off as θ increases (Figure 3d).

Similar plots were obtained for Na^+/Ag^+ diffusing into (Ag/Na) β''-alumina. For Yb^{3+} diffusing into $YBa_2Cu_3O_{6+\delta}$, the overlap of the barium fluorescence with that of the ytterbium made it impossible to obtain a reliable indication of ytterbium concentration, and only the yttrium concentration plot could be reliably analyzed.

Before analyzing the results in more detail, it is important to consider whether the observed directional nature of the

diffusion coefficient might be an experimental artifact. Possible sources for the anisotropy are:

1. "smearing" of the sample during polishing
2. nonorthogonal sectioning of the sample
3. "hot-spots" at the points of maximum diffusion

The consistency with which the diffusion is apparently enhanced parallel with the field gives a strong indication that the effect is not due to some directionality that may have been introduced at, for example, the sample preparation stage. If this were the case, then the anisotropy would be randomly oriented to the applied polarization. Furthermore, the enhancement would occur in only one direction, and a reduction in the apparent rate of diffusion would be observed at an angle of 180° to the enhancement.

The differences in the rate of diffusion could be explained by a cross-sectioning process that is not orthogonal to the major axis. In such a case, the cross section would be elliptical, and the diffusion zone on the major axis of such an ellipse would appear to be larger than those observed on the minor axis. The result would be an apparently larger diffusion constant along the major axis. However, for such an effect to give, for example, an apparent doubling in the diffusion coefficient requires the sample to be cut at an angle
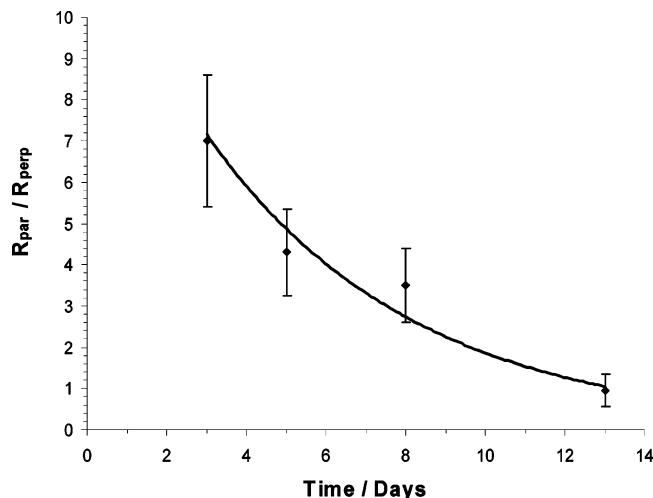
Figure 4. Diffusion enhancement as a function of processing time for the YbBa$_2$Cu$_3$O$_{7-\delta}$/YBa$_2$Cu$_3$O$_{7-\delta}$ system at ca. 700 °C.

of 60° to the longitudinal sample axis. The precision of the cut was determined to be 90 ± 0.5°, and such a large deviation from the orthogonal would be obvious to the naked eye. Furthermore, it is highly improbable that the sections in all the samples should be consistently misaligned so as to indicate enhanced diffusion *with* the microwave polarization.

Although the experimental arrangement was designed to minimize inhomogeneous heating through the use of small samples and homogeneous microwave fields, it is not possible to entirely discount this as a source of anisotropy. However, under the experimental conditions used, the position of "hot spots" is heavily dependent upon the dielectric properties of the materials used. In the experiments described here, both (Y/Yb)Ba$_2$Cu$_3$O$_{7-\delta}$ and (Na/Ag)-β''-alumina samples would have to exhibit a similar pattern of inhomogeneous heating, despite markedly different dielectric properties ($\epsilon' \approx 5.5$ and 2.5, respectively). The time dependence of the enhanced diffusion (*v.i.*) also indicates that macroscopic inhomogeneous heating is not the source of the anisotropy.

3.2. Temporal Dependence of the Diffusion Rate. By analysis of several samples of the same composition that had been exposed, for varying lengths of time, to otherwise identical experimental conditions, it is possible to obtain information about the time dependence of the diffusion enhancement. The simplest comparison is the ratio of diffusion coefficients for motion parallel with (R_{par}), and perpendicular to (R_{perp}), the applied field as a function of time. In Figure 4, the ratio, R_{par}/R_{perp}, of the two perpendicular diffusion coefficients are plotted as a function of processing time. This plot shows a clear decrease in the manifested effect of the microwave field as extended processing times are employed. It is clear that, irrespective of the nature of the effect, it is most significant at the start of the process. As the processing time increases, R_{par}/R_{perp} decreases as R_{par} reduces toward a thermally induced level.

With increased processing time, R_{par}/R_{perp} decreases toward an asymptotic limit of 1, indicating that the instantaneous R_{par} and R_{perp} become equal after a relatively short period and that prolonged microwave heating only serves to equalize the measured rates by reducing the significance of the

contribution from the initial enhancement. In later stages of sintering, the significance of thermal energy on ion motion in this direction is now as significant as the combined effect of thermal and microwave effects on R_{par}. In other words, the microwave influence decreases with time, almost certainly as a consequence of changes in the nature of the sample microstructure. At the start of the sintering process, the sample grains are only in close physical contact, and the diffusion enhancement diminishes as the grains fuse together.

Although early claims for nonthermal effects were generally nonspecific in their explanations, there have been enormous improvements in the theories that purpose to explain the microwave-sintering phenomenon. Early references to the microwave electric field having an influence on the size of the potential barrier between lattice sites has easily discarded, as the required field strengths ($>10^7$ Vm^{-1}) are significantly above that required to damage the sample.[34] Probably one of the most important hypotheses in the understanding of nonthermal effects in microwave-heated solids is that by Rybakov et al.[35−38] The enhanced ion transport and related effects explained in terms of a "solid-state ponderomotive force" and have been modeled as a consequence of gradients in the mobility of mobile charged species at or near grain boundaries or other physical interfaces.[37] Intense microwave electric fields, calculated to be several orders of magnitude greater than that in the rest of the sample,[39] are shown to induce a nonlinear driving force for the mass transport of charged species at these interfaces. Most notably, the microwave enhancement has been explained in terms of a "nonthermal" model that demonstrates the existence of a solid-state ponderomotive force, which enhances vacancy transport through second-order effects resulting from the time varying microwave electric field at the grain interfaces. While the existence of a ponderomotive effect is unequivocal and has been shown to operate in microwave-irradiated ceramics,[13] only indirect evidence of its influence upon sintering has existed to date.

It should be stated that, in this analysis, the assumption is made that the effect is an enhancement with the microwave field and not a suppression of diffusion perpendicular to it. Although the results described do not allow determination of which of these possibilities is correct, the numerous observations of enhanced sintering rates in similar ceramics point to the probability that an enhancement is being observed, rather than suppression. This approach is not only consistent with experimental observations but it is also open to more plausible explanation.

Although the sample, as a whole, will contain a complex electric field microstructure, it is possible to make some

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simplifying assumptions in the analysis of the areas under consideration. The mean field that is experienced by any pair of contacting particles can be approximated to that of a two-particle system embedded within a continuous dielectric matrix. The mean polarization of the field, when obtained from a number of samples at the same angle, θ, to the applied polarization will be approximately that of the applied field. By use of this assumption, we may compare the observed effect with a theoretical system that has been previously modelled. The microstructures within a ceramic have been shown, within a two-body system of ZnO or Al_2O_3 particles, to concentrate the local electric field into the interparticle contact regions.[39] The significant result is that the strength of the effect being dependent upon the angle between the field polarization and the interparticle axis. Although the dielectric properties of the materials are quite different, there is a clear similarity between the theoretical and experimental results. These results therefore indicate that there is an additional driving force that operates to enhance diffusion in the sample under microwave irradiation as a function of $|E|^2$. Within the context of these results, it is possible to interpret this fact in two possible ways.

First, if the model of a ponderomotive driving force (PMF) is considered, this influence is calculated to be a function of both the sample permittivity, ϵ, and the strengths of the high-frequency fluctuating electric field, E

$$PMF \propto \left\langle \frac{\epsilon}{2} \frac{\partial |E^2|}{\partial x} \right\rangle$$

This is in good agreement with the relation that is observed between the early diffusion enhancement and the strength of the electric field as a function of angle to the interparticle interface (Figure 4). According to the ponderomotive model, it is this driving force that enhances the transport of charged species, including vacancies, and so influences the reaction kinetics in heterogeneous solid-state reactions.[36] The presence of defects is important in both the transport of ions and in the dielectric properties,[40] and it seems that one of the most important functions of impurities is in increasing the concentration of lattice defects that, in turn, allow ion transport and contribute to the conduction component of the dielectric loss factor.[41−43] Clearly, in this model, as sintering times increase the distinct character of the grain boundaries are lost and the significance of the ponderomotive force will be diminished. Although it has been suggested that interfaces are not necessary for enhanced diffusion,[25] these results suggest that their presence represents a highly significant contribution to the microwave enhancement of mass transport in the sintering process.

It could be argued that it is possible to interpret the results in terms of a highly localized heating effect at the intergrain interface. The temperature of a particular volume of the sample under microwave irradiation is determined by the relative rate of energy flow in to and out of the volume and its analysis is not trivial.[44,45] However, the rate of energy flow, P, into the sample is dependent upon the square of the electric field strength

$$P \propto \epsilon_o \epsilon'' |E|^2$$

If the temperature variation of the heat capacity and energy transfer could be ignored, the local temperature, and hence the diffusion coefficient within the sample, would also be proportional to $|E|^2$. However, the rate of heat variations in the rate of energy transfer are mitigated by the rate of heat flow thought the system and detailed study of this relationship shows that the thermal gradients required could not be maintained across ceramic grains with micrometer-scale dimensions.[32]

4. Conclusions

The majority of solid-state processing or synthesis at high temperatures involves at least one of three stages namely, combination of the reactants, homogenization (annealing) of the product, and densification. Microwave heating has demonstrated advantages over conventional methods[6] in all three of these areas, principally because microwave heating is not dependent on conductive heat transfer within the solid.

The evidence supporting a microwave-specific contribution to these advantages is essentially limited to a solid-state PMF. The results presented in this work, which are entirely consistent with the PMF model, provide the first direct and unequivocal evidence that microwaves may directly influence ion transport in a high temperature sintering process. The electric field component of the microwave radiation is concentrated at the interparticle boundaries and the strength of the effect has a high dependence on the direction of the electric field. As the effect of this intense field is to concentrate the lattice defects and enhance ion mobility at the interface, then the rate of mass transport at a given temperature will be enhanced by the presence of microwaves. If this is indeed the case, then there may be implications for reduced energy use in solid state processing, and especially for the rate at which thermally sensitive materials may be processed.

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