Enhanced diffusion in sapphire during microwave heating

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The diffusion of oxygen in sapphire was accelerated by heating in a 28 GHz microwave furnace as compared with heating in a conventional furnace. Tracer diffusion experiments were conducted using ^{18}O. Single crystal sapphire wafers with a $(10\bar{1}2)$ rhombohedral planar orientation were used as the substrate. Concentration depth profiling was done by proton activation analysis using a 5 MeV Van de Graaff accelerator. The diffusion of ^{18}O was greatly enhanced by microwave heating as compared with conventional heating in the 1500–1800 °C range. The apparent activation energy for ^{18}O bulk diffusion was determined to be 390 kJ mol^{-1} with microwave heating and 650 kJ mol^{-1} with conventional heating.

1. Introduction

Microwave heating of ceramics has been demonstrated to enhance sintering, grain growth, and solid state reactions in a variety of ceramic systems [1–17]. Sintering is accelerated in alumina, zirconia, alumina–zirconia composites, and silicon nitride [1–11]. The temperature required to achieve a given sintered density is lower for microwave heating than for conventional heating in these systems. The magnitude of this temperature differential is often used as a measure of the enhancement caused by microwave processing. Temperature differentials as high as 400 °C have been reported [1, 2]. The magnitude of the differential depends on the material being processed and on the frequency of the microwaves being used. For sintering of alumina and silicon nitride, the "microwave effect" is larger at 28 GHz than at 2.45 GHz [1–4, 8, 9, 11]. Enhanced kinetics have also been demonstrated for grain growth in alumina [10] and silicon nitride [8], for solid state reactions [13–15], and for ion exchange in glasses [16, 17].

It has been hypothesized that the enhancement of the kinetics of sintering and grain growth in alumina is caused by microwave-enhanced diffusion. However, the evidence to date for microwave-enhanced diffusion in alumina is based on secondary effects; no direct measurements of diffusion in alumina have been made. Also, it is not clear from the reports in the literature whether bulk diffusion, grain boundary diffusion or both are enhanced by microwave heating. Furthermore, it has been shown in at least four cases [2, 5, 10, 11] that the apparent activation energy for sintering or grain growth in high-purity alumina is lower for microwave heating than for conventional heating.

There is a critical need to develop a better phenomenological understanding of the role of microwave heating in accelerating the kinetics of high temperature processes. Simpler phenomena need to be studied than sintering or grain growth. In sintering, many mechanisms occur simultaneously, including volume diffusion, grain boundary diffusion, and surface diffusion. In grain growth, the primary event is the jumping of an ion across a grain boundary, which is not equivalent to the movement of an ion along a grain boundary, which is grain boundary diffusion.

The most straightforward experiment would be to follow the diffusion of a particular ionic species into the bulk of a single crystal. However, even this approach requires careful consideration because of the special situations provided by the microwave environment. In microwave processing, not only the thermal properties of a material need to be considered; its dielectric loss properties must also be considered.

Consider a diffusion couple made by putting together a low dielectric loss material and a high loss material. Microwave power is absorbed differentially in the two halves of the couple according to the lossiness and the volume of each component [18]. Consequently, that half of the diffusion couple having the higher loss will absorb a larger fraction of the incident microwave energy than will the half of the couple having the lower loss. This difference in energy absorption will cause differential heating of the two halves of the couple. Differential heating will produce a temperature gradient across the diffusion couple even at steady state. Such a temperature gradient would seriously jeopardize the interpretation of the experiment since the couple would not be isothermal. Therefore, the study of hetero-ion diffusion in a material would have to be approached very carefully to make sure that the microwaves heat all regions of the sample uniformly. The most desirable case would be for all the materials involved in the experiment to have the same dielectric properties; i.e., the doped regions and the undoped regions of the couple. It is suggested

that the best approach to studying diffusion in materials during microwave heating is to use tracer ions that are isotopes of the ions that comprise the material chosen for study. This would guarantee that the dielectric properties of the doped and undoped regions would be as similar as possible.

The purpose of the present study was to directly demonstrate the presence or absence of microwave-enhanced kinetics for diffusion in a ceramic system. Aluminium oxide (sapphire) was chosen as the matrix material because previous studies of sintering [1–5] and grain growth [10] had reported that a "microwave effect" was obtained in this system. The stable isotope ^{18}O was chosen as the diffusing species. Thus, the doped and undoped regions of the sample had similar chemical and dielectric properties.

2. Experimental procedure
2.1. Furnace
Microwave heating was accomplished in a quasi-optical, 28 GHz microwave cavity that was designed and built at the Oak Ridge National Laboratory. Design and construction of the cavity have been discussed previously [7, 18, 19]. The primary point of importance regarding the microwave furnace is that the microwave field is extremely uniform inside it. For the worst case condition of an empty cavity, the point to point microwave field uniformity was better than $\pm 4\%$ [18, 19].

Microwave annealing was performed under vacuum (turbopump, pressure 7×10^{-3} Pa) at temperatures between 1500–1600 °C. Conventional annealing was performed in a tungsten element furnace (R. D. Brew and Co., Concord NH USA) under vacuum (diffusion pump, pressure $< 1.3 \times 10^{-3}$ Pa) at temperatures between 1700–1800 °C. All of the samples were annealed in covered crucibles having an identical composition to the samples. The crucibles were made from 99.999% purity alumina (AKP50, Sumitomo Chemical America Inc., NY, NY) with no additives. The temperature was measured using Type C thermocouples inserted into the crucibles. The bead of the thermocouple was placed within ≈ 1 mm of the sample. Sintering experiments had been conducted prior to these diffusion experiments [1, 2]. In those experiments, samples having uniform microstructures were obtained. There were no gradients in either grain size or density across samples that were ~ 2.5 cm in diameter and ~ 2.5 cm high. Because microstructure is a sensitive indicator of thermal history, we concluded that heating of samples inside this furnace was accomplished in a uniform manner.

A key element in conducting the microwave annealing experiments was the development of a technique for running small (~ 1 g) samples in the 28 GHz microwave furnace. For the sintering experiments that were conducted previously [1, 2], a sample size of ~ 120 g was used. Such a large sample was necessary to ensure correct and repeatable temperature measurements. Using such large samples for the diffusion experiments, however, would have been prohibitive. To solve the problem, a "ballast/crucible"
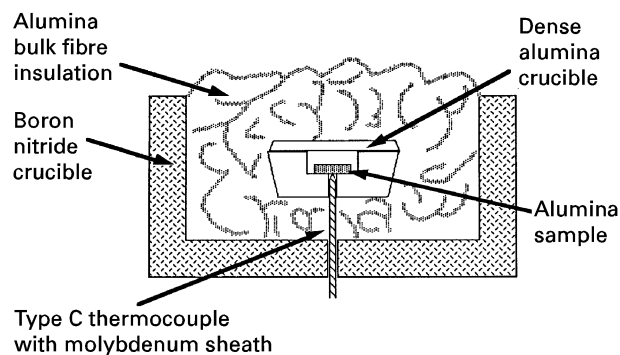

Figure 1 Schematic arrangement of sample and ballast/crucible in the 28 GHz microwave furnace.

arrangement was developed. In this arrangement, Fig. 1, a large crucible with lid (~ 150 g total mass) is made that has the same composition as the small samples that are to be run. The small samples are placed in a cavity in the crucible. On exposure to the microwave field, the sample becomes part of the total load in the furnace. In this way, coupling to the small sample can be accomplished that is equivalent to that achieved in a large sample. Sintering experiments were conducted using small samples (~ 5 g) in the "ballast/crucible" arrangement to demonstrate that microwaves would interact with the sample. The small samples in the "ballast/crucible" arrangement sintered to the same densities at the same temperatures as did the large (120 g) samples, which indicated the microwaves were indeed penetrating the crucible and interacting directly with the samples.

2.2. Temperature measurement
A major concern in conducting microwave furnace experiments is ascertaining that temperature is measured properly. Because the sample is heated directly by the microwaves (and not by indirect methods such as radiation, conduction, or convection), temperature measurement must be made within the sample, and not simply near the sample. This necessitates either inserting a thermocouple into the sample, as was done in this investigation, or using a sample containing a black-body hole if measurement is to be achieved using an optical or infrared pyrometer. In either case, measurement of temperature in a microwave furnace is non-trivial. Problems arise for both thermocouples and optical or infrared pyrometers. Thermocouples must be enclosed in a metallic protection sheath to shield the fine thermocouple wires from the effects of the microwave field. Unprotected wires arc and heat to their melting point in short order. By using a metallic protection sheath, the thermocouple wires are shielded from the effects of the microwaves because the electric field cannot penetrate the metal sheath. Fig. 2 shows the variation in time of both the electric field and the sample temperature (as indicated by a Type-C thermocouple embedded in an alumina part) in a 28 GHz microwave furnace. As the microwave electric field is cycled off and on, the thermocouple signal responds with decreasing,
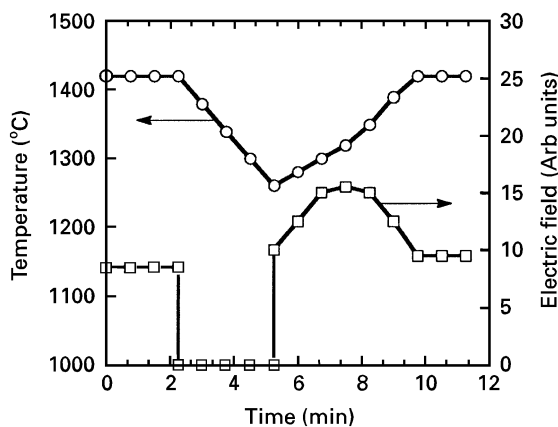
Figure 2 Turning the electric field on and off had no effect on the temperature recorded by the Type C thermocouple other than normal heating and cooling.

then increasing, temperature. However, there are no discontinuities in the temperature measurement when the power is turned off or on; this shows that the microwave field has no effect on the temperature measurement as made by the thermocouple. Only normal heating and cooling effects are observed, which are similar to those that would be observed in a conventional furnace if the power were turned off and on.

Recently, studies particular to the measurement of temperature in a 2.4 GHz microwave furnace have been conducted [20, 21], Excellent agreement (typically $\pm 20\,^\circ\mathrm{C}$) among three temperature measurement devices (thermocouple, 2-colour IR pyrometer, and fibre optic light pipe) was demonstrated over the range 500–1500 $^\circ\mathrm{C}$ for silicon carbide, silicon/silicon nitride, alumina, and zirconia samples. The silicon nitridation case [21] is especially instructive. In those experiments, there was excellent agreement between an IR pyrometer and a thermocouple ($\pm 10\,^\circ\mathrm{C}$). Additional confirmation of the temperature was based on the melting point of silicon. In tests where the thermocouple and pyrometer indicated that the temperture of the sample during nitridation was held below the melting point of silicon (1410 $^\circ\mathrm{C}$), there was no evidence that silicon had melted during processing. However, in tests where the thermocouple and the pyrometer indicated that the sample temperature had exceeded the melting point of silicon, large pools of silicon that had melted during processing were observed in the fired part. Thus, there was a three-way confirmation of the temperature to the part during processing – thermocouple, pyrometer, and presence or absence of melted silicon.

2.3. Sample preparation
The $^{18}\mathrm{O}$ source was synthesized in-house by hydrolysing aluminium isopropoxide with $^{18}\mathrm{O}$-enriched water (ICON, Mt Marion, NY) in ethanol using the procedure of Kim *et al.* [22]. The $^{18}\mathrm{O}$-enriched alumina powder thus produced was pressed into a compact and sintered to $\sim 98\%$ theoretical density. This dense alumina specimen was then used as the

target for electron beam deposition of the $^{18}\mathrm{O}$-enriched alumina onto the sapphire substrates used for the diffusion experiments. Commercial electronic grade sapphire (Union Carbide Crystal Products, Washougal, WA) cut parallel to the $(10\bar{1}2)$ crystal plane was used as the diffusion substrate. The diffusion direction was normal to the $(10\bar{1}2)$ plane. Commercial sapphire of this type has been used in previous investigations [23, 24]. The sapphire was already polished when received. Coupons 1×1 cm square were cut from the sapphire wafers. Before coating with the $^{18}\mathrm{O}$-enriched alumina tracer, the coupons were annealed at 1800 $^\circ\mathrm{C}$ for 4 h to reduce the amount of residual polishing damage present in the surface of the samples. For the sapphire samples, removing residual mechanical damage by annealing was considered quite important. This would tend to eliminate diffusion associated with dislocations, which is much faster than diffusion through the bulk of the crystal. A similar anneal was used by both Cooper and Reddy [23] and Reed and Wuensch [24] to eliminate non-Fickian diffusion profiles in their sapphire diffusion studies.

The samples were diffusion annealed in pairs, with the tracer-coated sides facing one another. This arrangement was used to minimize the amount of tracer lost due to evaporation and surface diffusion.

2.4. $^{18}\mathrm{O}$ analysis
Depth profiling of the $^{18}\mathrm{O}$ concentration was performed using proton activation analysis. The samples to be analysed were bombarded with 750 KeV protons in a Van de Graaff accelerator to promote the reaction:

$$^{18}\mathrm{O} + {}^{1}\mathrm{H} \rightarrow {}^{4}\mathrm{He} + {}^{15}\mathrm{N} \qquad (1)$$
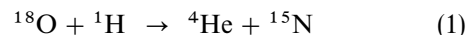
The scattered ions were collected by a surface barrier detector at a scattering angle of 145°. Detected events were energy analysed. By using the deconvolution technique of Lewis [25], the $^{18}\mathrm{O}$ depth profile was determined from the energy spectrum of the scattered $^{4}\mathrm{He}$ particles. Concentration profiling could be performed to a depth of 2 μm using this technique, with a precision of ~ 0.05 μm.

2.5. Data reduction
The thin film solution to the diffusion equation was used to analyse the concentration depth profile and to determine the diffusion coefficients from those profiles. The thin-film solution is given by Crank [26]:

$$\ln C(x,t) = \ln[M/(2\pi Dt)^{1/2}] - x^2/(4Dt) \qquad (2)$$

where: M = total amount of the diffusing species (mol)
D = diffusion coefficient (m^2 s^{-1})
t = time (s)
x = diffusion distance (m)
C = concentration (%)
A graph of $\ln[^{18}\mathrm{O}]$ versus x^2 should be a straight line with slope, $m = 1/(4Dt)$, from which the diffusion coefficient can be determined.

Use of the thin film solution is not strictly rigorous in the analysis of the diffusion coefficient from the

TABLE I Comparision of diffusion coefficients calculated using the thick-film and thin-film solutions to the diffusion equation for the data of Reed and Wuensch [24]

Temp (°C)	D (thick)	D (thin)	D (thick)/(thin)
1585	8.3×10^{-21}	4.5×10^{-21}	1.8
1620	1.25×10^{-20}	1.0×10^{-20}	1.25
1675	8.0×10^{-20}	5.8×10^{-20}	1.4
1840	2.2×10^{-18}	1.8×10^{-18}	1.2

depth–concentration data contained in this study. The initial thickness of the tracer layer (~ 0.2 μm) was not negligible relative to the diffusion distance achieved during annealing of the samples (~ 1 μm), which is a requirement for the thin-film solution to be strictly valid. Instead, a thick-film analysis should be applied if the best accuracy is to be obtained [24]. However, the estimate of the diffusion coefficient obtained from using the thin film solution is less than a factor of 2 different from that derived from the rigorous thick-film solution. This is demonstrated by the data contained in Table I. Here, the concentration versus depth data of Reed and Wuensch [24] were re-analysed assuming that the thin film solution could be used. As demonstrated in Table I, the difference in diffusion coefficient calculated by the two methods was within a factor of 1.2 to 1.8 for all cases. Furthermore, the activation energies (E_A) for diffusion calculated from the two sets of data were within 5% of one another (E_A[thin] = 780 kJ mol^{-1}; E_A[thick] = 740 kJ mol^{-1}). The purpose of this investigation was to compare conventional diffusion to microwave-assisted diffusion. Use of the thin-film approximation was deemed appropriate for these experiments. It provided an excellent measure of the *relative* diffusion coefficients, and a fairly good measure of the *absolute* diffusion coefficients, for ^{18}O in sapphire under both microwave and conventional conditions.

Data reduction was accomplished using the Stat-Works® statistical package (Cricket Software, Inc., Malvern, PA) for calculating the linear regression line and the correlation coefficient of the ln $[^{18}O]$ versus x^2 lines. The standard deviation of the slope of the regression line was calculated according to standard formulae [27] to give the 3σ confidence limits on the diffusion coefficients.

3. Results

Concentration–depth profiles for ^{18}O diffusion in sapphire were determined between 1500–1600 °C for microwave heating and at 1700–1800 °C for conventional heating. Different temperature ranges were chosen for microwave and conventional annealing because we anticipated that diffusion would be significantly higher in the microwave case. We were attempting to develop similar concentration–depth profiles for the two cases so that our analytical technique could be the same in both cases.

The depth profiles that were obtained followed the thin film model with a plot of ln $[^{18}O]$ versus x^2 being generally linear. Typical data for samples annealed at

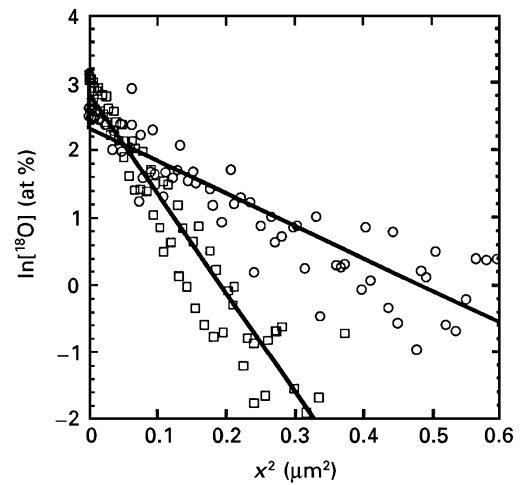*Figure 3* Concentration–depth profile for diffusion data of ^{18}O into sapphire plotted according to the thin film solution to the diffusion equation. (○) 1550 °C microwave anneal, 4 h hold; (□) 1750 °C conventional anneal, 4 h hold.

1550 °C for 4 h in the microwave furnace and at 1750 °C for 4 h in the conventional furnace are shown in Fig. 3. These data are typical for all of the diffusion experiments. The penetration of the ^{18}O tracer is significantly greater for the microwave case as compared to the conventional case, even though the temperature is 200 °C lower in the microwave case. Because the data are plotted according to the thin-film solution to the diffusion equation, ln $[^{18}O]$ versus x^2, the slope of the concentration–depth line is proportional to $1/D$. Hence, the smaller slope of the microwave line indicates that its diffusion coefficient is higher. Similar analyses were made for all of the diffusion runs. The results are summarized in tabular form in Table II.

The diffusion coefficients for both the microwave and conventional heating conditions are presented in standard Arrhenius form ($D^* = D_0 \exp[E_A/RT]$) in Fig. 4, where D^* = tracer diffusion coefficient, D_0 = pre-exponential factor, E_A = apparent activation energy for tracer diffusion R = gas constant, and T = absolute temperature. The best-fit equations for the two cases are given by:

Conventional (ORNL):

$$D^*(m^2 s^{-1}) = 9.7 \times 10^{-2}(m^2 s^{-1})$$

$$\exp[-650 \text{ kJ per mol per } RT]$$

TABLE II Trace diffusion coefficients for ^{18}O diffusion in sapphire under microwave and conventional annealing conditions

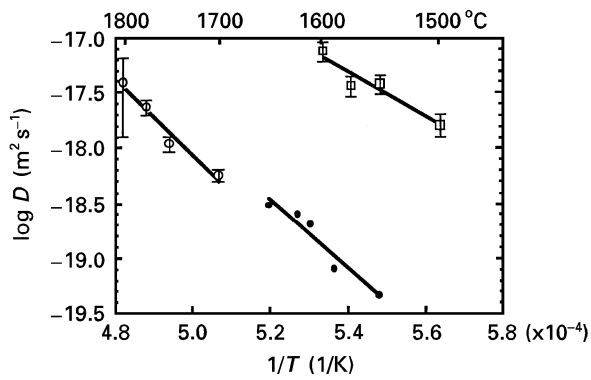| Temperature (°C)	Microwave $\times 10^{-18}$ (m^2 s^{-1})	Conventional $\times 10^{-18}$ (m^2 s^{-1})
1500	1.6	
1550	3.7	
1575	3.6	
1600	7.4	
1700		0.58
1750		1.1
1775		2.3
1800		3.8

Figure 4 The apparent activation energy for diffusion of ^{18}O in sapphire was lower for microwave firing as compared with conventional firing. Diffusion was perpendicular to the $(10\bar{1}2)$ rhombohedral plane. Error bars indicate 3σ limits on the estimates of the diffusion coefficients. (●) is the data of Reddy and Cooper [23] with an activation energy of 615 kJ mol^{-1}, (□) is the ORNL MW data with an activation energy of 385 kJ mol^{-1} and (○) is the ORNL conventional data with an activation energy of 650 kJ mol^{-1}.

Microwave (ORNL):

$$D^*(\text{m}^2\,\text{s}^{-1}) = 3.8 \times 10^{-7}(\text{m}^2\,\text{s}^{-1})$$

$$\times \exp[-390\,\text{kJ per mol per } RT]$$

The data of Reddy and Cooper [23], which are typical of other data in the literature, which were determined using the same type and orientation of sapphire crystal, and which used proton activation analysis for depth profiling are included for comparison. For their data, the best-fit equation is given by:

Reddy and Cooper:

$$D^*(\text{m}^2\,\text{s}^{-1}) = 2.7 \times 10^{-2}(\text{m}^2\,\text{s}^{-1})$$

$$\times \exp[-615\,\text{kJ per mol per } RT]$$

The conventional diffusion coefficients from the present investigation are in good agreement with the data of Reddy and Cooper [23]. In contrast, the microwave diffusion coefficients from the present investigation are significantly higher than their conventional counterparts. These data demonstrate that diffusion of ^{18}O in sapphire progressed much faster in the microwave case as compared with the conventional case.

4. Discussion

The results given above demonstrate a significant effect of the microwave field on the diffusion of ^{18}O in single crystal sapphire. We now consider how these data compare with other diffusion studies, how they compare with previous studies of microwave processed ceramics, and what possible explanations there might be for the observed behaviour.

4.1. Comparison with other diffusion studies in sapphire

A summary of values for apparent activation energy (E_A) and pre-exponential factor (D_0) for ^{18}O diffusion in sapphire is given in Table III. The data were

TABLE III Comparison of pre-exponential factors, D_0, K_0, and R_0, and apparent activation energies, E_A, for diffusion, grain growth and sintering in sapphire and high-purity alumina in conventional and microwave furnaces

Investigation	Date	Type[a]	D_0 (m^2 s^{-1})	E_A (kJ mol^{-1})
^{18}O Diffusion in sapphire				
Oishi, Ando, and Kobota [28]	1980	3	1.1×10^{-1}	650
Reed and Wuensch [24]	1980	1	6.4×10^{1}	785
Reddy and Cooper [23]	1982	2	2.7×10^{-2}	615
Oishi, Ando, Suga and Kingery [29]	1983	3	5.6×10^{-2}	665
Lagerlof, Mitchell, and Heuer [30]	1989	4	6.8×10^{-4}	590
ORNL Conventional	Present Study	1	9.7×10^{-2}	650
ORNL MW (28 GHz)	Present Study	1	3.8×10^{-7}	390
Grain growth in alumina			K_0 (µm^3 s^{-1})	
ORNL Conventional [10]	1991		1.3×10^{-4}	590
ORNL MW (28 GHz) [10]	1991		2.5×10^{-6}	480
Sintering in alumina			R_0 (% per s)	
Coble[b] [31]	1958		NA	690
Bykov *et al.* MW (83 GHz) [5]	1990		NA	100
ORNL Conventional[c] [2]	1990		2.2×10^{36}	575
ORNL MW (28 GHz)[d] [2]	1990		2.0×10^{14}	170
EA Tech MW (2.45 GHz) [11]	1992		NA[d]	240

[a] Type of experiment used to determine diffusion coefficients.
1 – Al$_2$$^{18}O_3$ tracer deposited on $(10\bar{1}2)$ face of single crystal.
2 – ^{18}O gas-exchange with $(10\bar{1}2)$ face of single crystal.
3 – ^{18}O gas-exchange with crushed sapphire particles.
4 – Annealing of dislocation loops; assumes dislocation climb is controlled solely by oxygen diffusion.
[b] Initial stage sintering
[c] Intermediate stage sintering
[d] While data are not available in the open literature, private communication with staff at EA Technologies, Ltd., confirmed that the pre-exponential factor was many orders of magnitude lower for microwave sintering as compared with conventional sintering.

gathered using a wide range of techniques by several different research groups. While the list is not exhaustive, it is representative of the literature in the field. Also included in Table III are apparent activation energy data for conventional sintering of alumina, conventional and microwave studies of grain growth in alumina, and conventional and microwave (2.45 GHz, 28 GHz, and 83 GHz) sintering of alumina.

The following major points can be noted from Table III. Most of the measured apparent activation energies for diffusion of ^{18}O in sapphire under conventional heating conditions are in the range 590–665 kJ mol^{-1}, with only one value above 665 kJ mol^{-1} (Reed and Wuensch, 785 kJ mol^{-1}). All of the conventional pre-exponential factors are similar (in the range $\sim 10^{-3}- \sim 10^{-1}$ m^2 s^{-1}) with only one exception (Reed and Wuensch, 6.4×10^1 m^2 s^{-1}). The values determined under conventional heating conditions in the present investigation, $E_A = 650$ kJ mol^{-1} and $D_0 = 9.7 \times 10^{-2}$ m^2 s^{-1}, were in good agreement with the literature values. In contrast, for diffusion of ^{18}O in sapphire under microwave (28 GHz) heating conditions, both the measured activation energy and the pre-exponential factor were significantly lower than their conventional counterparts, $E_A = 390$ kJ mol^{-1} and $D_0 = 3.8 \times 10^{-7}$ m^2 s^{-1}. The apparent activation energy was only 60% of the conventional value and the pre-exponential factor was about five orders of magnitude lower than the conventional value.

4.2. Enhanced diffusion in the microwave field

The data in Table III show that the values of apparent activation energy and pre-exponential factor measured at ORNL for conventional sintering, grain growth, and diffusion are in reasonable agreement with those reported by other researchers. One can conclude from this that the experimental techniques used in the present investigation are reliable and accurate. The data in Table III and in Figs 3 and 4 also demonstrate that diffusion of oxygen in sapphire is significantly enhanced by microwave heating. One is left then with a question: Is the phenomenon of enhanced diffusion in sapphire real, and if so, what is the explanation for these unusual observations?

The most obvious explanation for the apparent increase in diffusion of oxygen in alumina is that the temperatures were measured incorrectly in the microwave furnace. The following discussion explores that argument more fully. Fig. 5 presents the data for microwave and conventional diffusion of ^{18}O in sapphire from the present investigation. Also shown are the microwave data replotted assuming that the temperature measurements in the microwave furnace were made incorrectly by increments of 100, 200, and 250 °C. The numbers next to the curves show the apparent activation energies for diffusion that would be obtained for each case. Fig. 5 shows that a temperature measurement error of 250 °C would be required to bring the microwave data into reasonable agreement with the conventional data. Good agreement
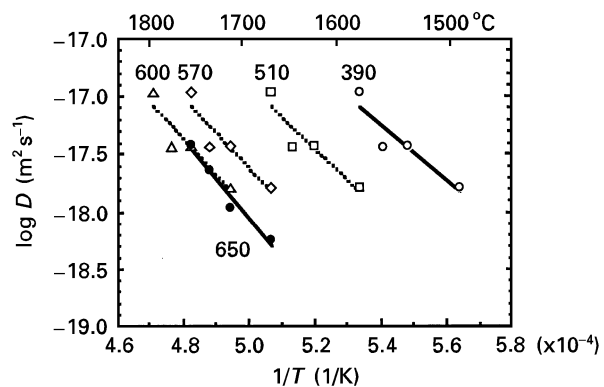

Figure 5 Diffusion data for ^{18}O in sapphire assuming different temperature measurement errors. The data for (○) microwave and (●) conventional annealing from the present investigation are shown by the solid lines. The microwave data have also been replotted assuming that the temperature measurements in the microwave furnace were in error by increments of (□) 100, (◇) 200, and (△) 250 °C. The numbers next to the curves indicate the apparent activations energies (kJ mol^{-1}) for diffusion in each of the cases.

between thermocouples and other techniques (IR pyrometer, melting point, or fibre optic probe) [20, 21] has been demonstrated in studies specifically designed to study temperature measurement in microwave furnaces. In the worst cases (typically at temperatures below 1000 °C), discrepancies between the thermocouple and other techniques are not larger than ± 50 °C. In the best cases, agreement is within ± 10 °C, which is as good as with temperature measurements in conventional furnaces. These discrepancies are significantly smaller than the 250 °C difference that would be required to explain away the increases in diffusivity observed in the present study.

If one accepts the temperature measurements in this investigation as valid, then one has to ask by what mechanism(s) could the diffusion of oxygen in alumina be enhanced. To investigate the possibilities, we turn to the mathematical formulation of the activation energy for diffusion.

The equation describing tracer diffusion (assuming a single, dominant defect mechanism such as Schottky, anion Frenkel, or cation Frenkel) is given by [32]:

$$D^* = 1/6 \, \Gamma^* \lambda^{*2} f_d^* \qquad (3)$$

where: $D^* =$ tracer ion diffusivity
$\Gamma^* =$ total jump frequency for tracer ions
$\lambda^* =$ jump distance for tracer ions
$f_d^* =$ tracer correlation factor for diffusion.
The total jump frequency is given by:

$$\Gamma^* = czw \qquad (4)$$

where: $c =$ mole fraction of defects ($\approx \exp - g^f/kT$, for intrinsic defects)
$g^f =$ free energy of formation of defect
$k =$ Boltzman's constant
$T =$ absolute temperature
$z =$ number of adjacent sites
$w =$ jump frequency of a single defect between two specified sites, which is given by –

$$w = v_0 \exp(- g^m/kT) \qquad (5)$$

where: g^m = free energy of activation for motion of the defect v_0 = attempt frequency ($\sim 10^{13}\,\text{s}^{-1}$).
Combining Equations (3–5) and collecting terms yields:

$$D^* = \{1/6\,z\lambda^{*2}f_d^* v_0 \exp(-[s^f + s^m]/k)\}$$
$$\times \exp(-[h^f + h^m]/kT) \qquad (6)$$

where: s = entropy of the defect (superscripts: f = formation, m = motion) h = enthalpy of the defect (superscripts: f = formation, m = motion).
The diffusion equation can be recast into a different form that can be related to the experimentally measured quantities, D_0 and E_A, such that:

$$D^* = D_0 \exp[-E_A/kT] \qquad (7)$$

By comparison with Equation 6 one can show that the pre-exponential factor is:

$$D_0 = 1/6z\lambda^{*2}f_d^* v_0 \exp(-[s^f + s^m]/k) \qquad (8)$$

and the apparent activation energy is;

$$E_A = [h^f + h^m] \qquad (9)$$

This form of the equation shows (1) that the pre-exponential factor, D_0, is a function of entropies of defect formation and defect migration as well as the number of adjacent sites, the jump distance, and the correlation factor, and (2) that the activation energy, E_A, is a function of the enthalpy of defect formation and migration.

In the present investigation, reduction of both D_0 and E_A was observed. The question, then, is what could the microwave field be doing to the system to produce such large changes in the observed diffusivity?

Consider first the pre-exponential factor, D_0. It is reasonable to assume that both the number of adjacent sites and the jump distance are not affected by the microwave field. This leaves the correlation factor and the entropies of formation and migration of the dominant defect type for consideration.

In concept, changes in the correlation factor could affect the value of D_0. However, even in extreme cases investigated by numerical simulation [33], changes in the correlation factor by more than a factor of 10 are highly unusual. In this investigation, D_0 changed by approximately 5 orders of magnitude, which is far larger than what might be expected from changes in the correlation factor.

Changes in the entropy of formation or the entropy of migration of the dominant defect could also change the value of D_0. Furthermore, because these values appear in an exponential term, small changes in either entropy term would be magnified in D_0. It is postulated that the microwave field would more likely have an effect on the migration of a defect than have an effect on its formation. A microwave photon is not energetic enough to have an effect on the formation of defects. However, the electric field associated with microwave processing might be strong enough to alter the conditions at the saddle point such that the jump event becomes easier.

Consider next the apparent activation energy for diffusion, E_A. As formulated in Equation 10, the activation energy is equal to the enthalpy of formation for the dominant defect plus the enthalpy of motion for that defect. Again, it is suggested that the microwave field is more likely to affect the motion of defects than to affect their formation.

4.3. Comparison with previous research on microwave processing of alumina

At least five research groups (ORNL [1, 2, 10], Asea-Brown Bovari [4], EA Technologies [11], Russian Institute of Applied Physics [5], University of Florida [9]) have observed enhanced sintering or enhanced grain growth in microwave-processed alumina, Table III. Three of these groups [1, 5, 10, 11] have reported a lower apparent activation energy for sintering or grain growth, Table III. In all of the cases, both the apparent activation energy and the pre-exponential factor were lower for microwave heating as compared with conventional heating. The present results for diffusion of ^{18}O in sapphire confirm the trends demonstrated in the earlier sintering and grain growth studies: diffusion is enhanced by processing in a microwave field.

There are differences in the activation energies for microwave-enhanced diffusion, sintering, and grain growth observed by the various research groups. These variations can be attributed to the differences in the processes that take place. The mechanisms that occur in diffusion, grain growth, and sintering are related; but, they are not identical. In the diffusion experiments, volume diffusion is the process in question; in grain growth, jumping of ions across a grain boundary; and in sintering a combination of surface, grain boundary, and volume diffusion with continuously changing boundary conditions. Since different processes are being studied, it should not be surprising that different activation energies are observed.

The results for sapphire show that volume diffusion is enhanced by microwave heating even in a pure single crystal. That is, neither free surfaces, porosity, nor grain boundary discontinuities are necessary for microwave enhancement of diffusion to be obtained. Therefore, arguments that (1) microwave-enhancement of kinetic processes in crystals must be based on electric field discontinuities at grain boundaries, pores, or free surfaces, or that (2) microwave enhancement could only apply to interfacial phenomena as have been made by some researchers [34, 35] are weakened. We suggest that the phenomenon of microwave-enhanced kinetics in a ceramic system depends on the direct interaction of the microwave field with the defects responsible for diffusion, i.e., vacancies and interstitials. In this way, the energy state of these defects might be elevated without affecting the overall temperature of the material.

4.4. Theoretical context of the research

No predictive theory of microwave-enhanced kinetics in ceramic systems exists at the present time. Several

different approaches [35, 36–39] have been explored. They include non-thermal phonon distributions, molecular dynamics simulations, bound versus free absorbers, and multiple scattering theory. Unfortunately, all of these attempts are preliminary, making first-order or even zeroth-order assumptions regarding the systems in questions.

The present work does not suggest an obvious path to developing a viable theory of microwave-enhanced kinetics in inorganic systems; however, this work, combined with previous research, can delineate what phenomena must be explained by such a theory. First and foremost, the theory must be able to explain why microwave heating enhances volume and grain boundary diffusion in alumina at 28 GHz and enhances ion exchange diffusion in glasses at 2.45 GHz. Next, it should address enhanced sintering of alumina, zirconia, and silicon nitride. Here, theory should not only deal with the accelerated densification observed, but also explain the differences in microstructure developed by microwave-processed samples such as smaller grain sizes at equivalent densities or different pore evolution paths obtained. These observations suggest that microwave heating enhances bulk and/or grain boundary diffusion more than it does surface diffusion. Furthermore, the theory should deal with the effect that frequency has on kinetics. For example, Table III shows that the apparent activation energy for sintering of alumina falls from 575 kJ mol^{-1} for conventional sintering to 240, 170, and 100 kJ mol^{-1} for microwave sintering at 2.45, 28, and 83 GHz, respectively. Similar phenomena have been observed for the sintering of silicon nitride at 2.45 and 28 GHz; i.e., silicon nitride densifies at a lower temperature at 28 GHz than at 2.45 GHz, both of which are lower than for conventional firing [8]. Finally, the theory should include an explanation of the role that dielectric loss plays in determining how much the kinetic processes in materials systems are affected by microwave heating. Several investigators [3, 6, 16, 17, 40] have demonstrated that the amount of sintering or ion exchange enhancement caused by microwave heating of oxide materials at 2.45 GHz is related to the lossiness of the material; the higher the dielectric loss, the greater the microwave enhancement. This macroscopic effect needs to be explained on an atomistic level.

Recently, Freeman et al. [41] have developed convincing evidence for a "microwave effect" in the NaCl system. They have demonstrated the existence of a microwave-induced ionic current in NaCl single crystals. They have shown that the magnitude of the microwave-induced current increases linearly with the microwave power applied, but it is independent of any applied bias voltage. Their analysis of the data suggests that the microwave field enhances the driving force for diffusion rather than either the mobility or the concentration of defects.

4.5. Relationship to other materials systems
Microwave heating has been demonstrated to accelerate kinetics in organic systems. Curing of epoxies and other polymer processes is enhanced [42, 43]; accelerated kinetics in the synthesis of numerous organic compounds [44] have been reported; and, accelerated diffusion of ethylene oxide through poly (vinyl chloride) polymer has been observed [45]. In two of these cases [43, 45] reduction in the apparent activation energy and pre-exponential factor for the process was reported. Lewis et al. [43] studied the imidization of poly (amic acid). The apparent activation energy for the reaction was reduced from 105 kJ mol^{-1} for conventional heating to 57 kJ mol^{-1} for microwave heating (45% reduction); the pre-exponential rate factor was reduced from 2.7×10^{10} to 4.4×10^{15} min^{-1} (5 orders of magnitude decrease). Similarly, Gibson et al. [45] reported a reduction in the apparent activation energy for diffusion of ethylene oxide through poly (vinyl chloride) from 57.3 to 28 kJ mol^{-1} (51% reduction) and a reduction in the pre-exponential factor from 2.73×10^{-3} to 1.7×10^{-7} m^{2}s^{-1} (4 orders of magnitude decrease). The changes in apparent activation energy and pre-exponential factor for these organic systems are similar in magnitude to that observed in the present study for diffusion in sapphire. Also, the simultaneous reduction of apparent activation energy and pre-exponential factor appear to be universal for systems that exhibit microwave-enhanced kinetics. Such behaviour has been observed for diffusion, grain growth, sintering and chemical reactions.

5. Conclusions
(1) Volume diffusion of ^{18}O in alumina was enhanced by heating in a 28 GHz microwave furnace.
(2) The apparent activation energy for volume diffusion was reduced by 40% from 650 to 390 kJ mol^{-1}. The pre-exponential factor was reduced by five orders of magnitude from 9.7×10^{-2} to 3.8×10^{-7} (m^{2}s^{-1}).
(3) The present results help to explain the accelerated kinetics observed during sintering and grain growth in the alumina, zirconia, and silicon nitride ceramic systems.
(4) The present results are consistent with those reported previously for microwave acceleration of ion-exchange in silicate glasses.

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