SINGLE-MODE MICROWAVE SINTERING OF Er:Al_2O_3

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INTRODUCTION

The application of intense AC/DC magnetic, electric, and acoustic energy during materials processing has been shown to influence crystal structure and microstructure phenomena such as texturing, nucleation, grain growth, phase transformation, grain boundary migration, segregation, diffusion, and densification [1,2]. Although electromagnetic (EM) fields are currently being utilized in a variety of materials processing approaches, in many cases a fundamental understanding of the underlying physics is still lacking. Despite the knowledge gap regarding materials response in EM fields, recent breakthroughs continue to demonstrate the critical role that EM fields can play in materials processing.

A basic advantage of this emerging class of processing techniques is the expanded processing space made possible by the introduction of novel processing parameters. One such technique is microwave sintering, in which microwave energy of different frequencies and fields is converted into heat. Whereas conventional processing techniques are largely confined to familiar experimental parameters (e.g. time, temperature, heating rates, environment, applied pressure), microwave sintering also adds all of the experimental variables inherent to EM radiation: frequency, mode (E and/or H), polarity, and intensity. During multi-mode microwave sintering, the most common microwave technology used in materials processing, microwave radiation is emitted into a reflective cavity that is much larger than the wavelength. Due to the randomized nature of the EM waves (due to wall reflection and intentionally included mode-stirrers), multiple modes are excited within the cavity. This design is intended to produce a mixed electromagnetic energy within the cavity. While this is beneficial for heating large objects uniformly, it inherently limits fundamental studies of the mechanisms by which microwave energy interacts with matter, since many modes are active in the chamber and the effects of electric and magnetic fields cannot be separated.

In addition to multi-mode microwave systems, which are commercially available and widely used in both industry and research, various researchers have developed single-mode microwave sintering systems. Through careful design of the applicator, the microwave radiation can form a standing wave (i.e. a single mode is excited). One advantage of this design is the significantly lower power requirements, since microwave energy is concentrated in only one or two modes in a small area of the cavity. Our interest lies in its ability to fully (spatially) separate the electric and magnetic field components of EM waves at specific cavity locations. Single-

mode microwave heating, therefore, holds great promise for fundamental research in microwave processing, since the electric and magnetic field maxima are separated spatially in the chamber. Hence, depending on the sample position, the sample can be subjected to 100% electric and 0% magnetic energy and vice versa. Earlier reports [3-5] have demonstrated that processing materials in the regions of electric field and magnetic field maxima in a single-mode microwave system can produce unique microstructures and phase transformations, and enable the processing of a wider range of materials.

While many studies have been performed in the regions of electric or magnetic maxima using single-mode microwave systems, the potential benefits of using mixed component microwave fields have gone largely unexplored. That is, in addition to the 100%:0% field ratios, the sample may be moved such that it experiences a non-zero percentage of both fields: a *mixed field* mode, e.g. 30% electric field and 70% magnetic field. This unique experimental parameter afforded by single-mode microwave sintering may provide insight into how the different fields affect crystal structure and microstructure-controlling mechanisms during such heat treatment. In addition, the ability to adjust the relative amounts of applied electric and magnetic fields may be especially useful for materials such as Al_2O_3, which is diamagnetic, and does not couple to the magnetic field, so the 100% magnetic field, 0% electric field condition does not heat the sample. Therefore, using the *mixed field* condition, one field can be utilized to heat the sample and the other field can be varied to study its effects on the material microstructure quasi-independently. The percentage of fields is based on the empty cavity, which may change slightly when a sample is placed in the field.

One structural characteristic of interest in materials processing is the incorporation of dopants, particularly rare earths that are not thermodynamically stable within the material of choice. For example, rare-earth doped ceramics with high thermal conductivity (such as Al_2O_3 and AlN) are currently being studied for transparent material applications. In order to obtain transparency in such materials (which tend to be non-cubic and contain small cations), the density must be high (near theoretical), the grain size must be small (< wavelength of light), and the refractive index mismatch between grains must be minimized. Microwave sintering has been shown to produce dense materials more rapidly than conventional sintering, thereby limiting the grain growth. In order to address the refractive index mismatch between grains, crystallographic texturing may be used. Rare earth (RE) dopants may increase the ability to orient powders in a magnetic field due to an increase in the magnetic susceptibility anisotropy. In fact, the magnetic anisotropy can be enhanced by incorporating low concentrations of RE ions by up to a factor of 10 [6,7].

This paper reports preliminary results from the sintering of RE-doped Al_2O_3 in multi- and single-mode microwave systems. Powders and sintered pellets were characterized via Archimedes density measurements, X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). The focus will be on the single-mode microwave sintering system and the effect of placing the sample in different positions along the cavity so that it experiences varying proportions of electric field and magnetic field. In order to study how the EM field at microwave frequencies (2.45 GHz) affects the sintering behavior of RE-doped Al_2O_3, microwave sintering parameters including the temperature, microwave frequency, and sintering atmosphere were held constant. The results show that the *mixed field* parameters have an effect on both the density of the sintered ceramic as well as the RE dopant migration.

EXPERIMENTAL PROCEDURE

In general, doping Al_2O_3 with RE ions is very challenging since RE cations are very large relative to the aluminum cations. Therefore it was necessary to synthesize Al_2O_3 with erbium (Er) as a dopant directly (as opposed to adding Er to commercially available Al_2O_3 powder). Aluminum oxide powders containing Er as the RE dopant were synthesized via co-precipitation. In this technique, an acidic solution (consisting of $Al(NO_3)_3.XH_2O$, $Er(NO_3)_3.XH_2O$, and $Mg(NO_3)_2.XH_2O$ in DI H_2O) and a basic solution (consisting of NH_4OH and NH_4HCO_3 in DI H_2O) were simultaneously added drop-wise into a buffer solution with a pH of 7. As the acidic and basic solutions were added to the buffer solution, doped aluminum hydroxide and aluminum carbonate particles precipitated out. Throughout the process the pH was maintained at 7. Because Er solubility within the Al_2O_3 crystal structure is so limited, any attempt to fabricate phase-pure Er:Al_2O_3 would require very low Er concentrations. Therefore, excess Er nitrate was added into the solution (resulting in 0.5 cation%) for these experiments to facilitate analysis of Er diffusion and/or secondary phase formation. By adding excess Er and monitoring second phase evolution, we hoped to gain an understanding of how the microwaves affect Er stability and migration, particularly in the *mixed field* microwave sintering experiments.

After the powders were precipitated, they were stirred overnight and washed/filtered with DI water twice and isopropyl alcohol once. The powders were dried overnight and crushed before calcination. The powders were calcined at 1360°C for 30 minutes, and XRD spectra were collected on the calcined powders to verify complete organic removal and quantify the phase content of the Al_2O_3 powder. Following calcination, the powder was jet-milled using a jet mill from The Jet Pulverizer Co., Inc. Jet milling was utilized to minimize the particle size without relying on the use of milling media, which may introduce contamination into the powders. Possible contamination sources must be carefully considered during powder fabrication and processing, since any secondary phases will enhance the scattering and decrease the transparency. Pellets of 13 mm in diameter were cold isostatically pressed to 400 MPa and then either conventionally sintered or microwave sintered.

To obtain baseline materials, two samples were pressure-less sintered, using a ramp rate of 15°C/min and a hold time of two hours. Microwave sintering was performed using either a 2 kW 2.45 GHz multi-mode system or a 2 kW 2.45 GHz single-mode system. The details of single-mode microwave system are given elsewhere [4]. The microwave sintering parameters, as well as the sintering parameters for the baseline samples, are shown in Table I (SM stands for single-mode microwave sintered, BL stands for baseline conventionally sintered, and MM stands for multimode microwave sintered). The SM samples also include indication of the relative amounts of the electric and magnetic field. For example, SM-100:0 was sintered at the center of the electric field maximum, where magnetic field was zero, while SM-30:70 is situated along the chamber axis where the ratio of electric and magnetic fields was estimated to be 30:70. All samples were sintered in air at 1400°C (with a two-hour hold). The temperature measurement was made using an optical pyrometer (Leeds & Northrup Co., Philadelphia, PA USA) focused on the surface of the sample. A typical heating schedule for the sample sintered at 1700°C was 30°C/min from R.T. to 1200°C, and 20°C/min from 1200°C to 1700°C.

After sintering, XRD patterns were measured on sintered pellets and ground powder samples using a Rigaku MiniFlex powder X-ray diffractometer and the spectra were analyzed using the commercial software, Jade 8. The peaks heights of the (420) plane for the $Er_3Al_5O_{12}$ phase and the (104) plane for the Al_2O_3 phase were carefully measured to determine relative second phase content (also given in Table I). Samples were prepared for electron microscopy by polishing with successively finer diamond films, down to a 6 µm polish. Following the mechanical polishing step, the samples were ion-polished in plan-view using a Leica TIC 3X ion

beam slope cutter on a rotary stage with a beam energy of 6 kV and a milling time of one hour. The ion polishing was used to remove any residual surface scratches from mechanical polishing, and to ensure that the pores did not become filled in with polishing compounds, which would obscure the appearance of the microstructure. The ion polishing step was especially useful in preparing the lower density samples, which contain many pores. The sintered ceramic pellets were observed using either a Hitachi 4700 FESEM at 1.5 kV or an FEI Nova NanoSEM 600 using the low-vacuum option (80 Pa), which is equipped with an Oxford EDS system.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for the starting (unsintered) powder as well as sample SM-30:70. The starting powder is composed primarily of α-Al_2O_3, with minor amounts of $ErAlO_3$ and θ-Al_2O_3. The presence of $ErAlO_3$ confirms that the solubility of Er had been exceeded, and that some Er, even at the low calcination time and temperature, had been allowed to diffuse out of the lattice and form an Er-rich second phase. The SM-30:70 sample shows peaks corresponding to α-Al_2O_3 as well as $Er_3Al_5O_{12}$. The inset shows the (420) plane for the $Er_3Al_5O_{12}$ phase and the (104) plane for the Al_2O_3 phase, which were used for the phase content calculations.

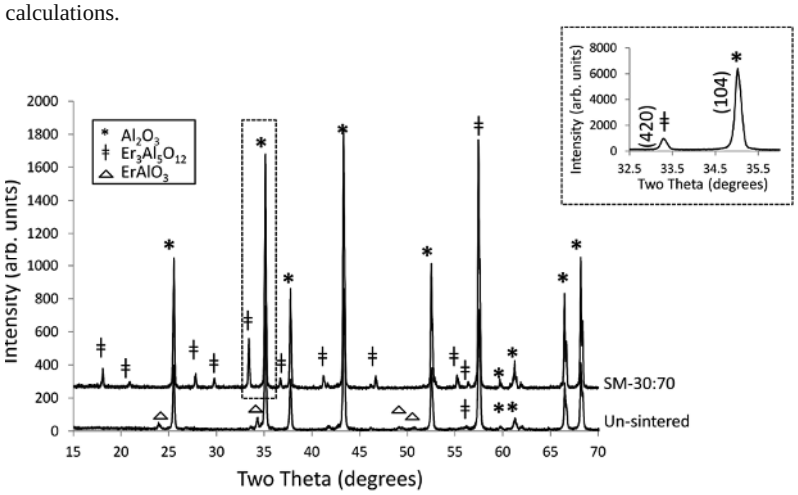

Figure 1. X-ray diffraction patterns for calcined Er:Al_2O_3 powder and sample microwave sintered sample SM-30:70. The inset shows the (420) peak of the $Er_3Al_5O_{12}$ phase and the (104) peak of the Al_2O_3 phase; these peaks were used to determine the peak height ratios given in Table I.

In order to establish a baseline material, we initially sintered the Er:Al_2O_3 powder using conventional (pressure-less) sintering (sample BL was sintered at 1400°C for 2 hr and sample BL-HT was sintered at 1650°C for 5 hr). As shown in Table I, the density for BL was quite low at 2.80 g/cm^3, which was ~70% of the theoretical density. Without the benefit of applied pressure or wet powder processing, this low density was not surprising. Most microwave processed samples had similar densities. SM-60:40 and SM-100:0 had similar densities compared to the conventionally sintered sample; the densities of these two microwave sintered samples were within 5% of the baseline sample. MM was slightly denser (2.93 g/cm^3). SM-

30:70, however, was significantly denser (3.88 g/cm^3, or about 97% of the theoretical density of Al_2O_3). The density of SM-30:70 was highly anomalous but also encouraging, since this density was comparable to densities achieved by hot-pressing Er-doped Al_2O_3 at 1350°C. Therefore, by using the 30%E:70%H microwave sintering condition, we could potentially eliminate the need for hot-pressing, and the only compromise would be an increased sintering temperature of 50°C (1350°C to 1400°C). In fact, SM-30:70 is similar in density to BL-HT despite the 250°C difference in temperature. If one assumes that BL-HT represents the maximum density possible within our samples (as limited by our particular powder and particle packing characteristics), then SM-30:70 achieved maximum density under thermal conditions *that would otherwise produce 70% dense samples*.

Table I. List of Sintering Conditions, Density and Phase Quantification for all Samples

Sample	Temp (°C)	Microwave Conditions	Density (g/cm^3)	Peak Height Ratio	Equivalent Vol%* $Er_3Al_5O_{12}$
BL	1400	No microwave	2.80	7.31	2.62
BL-HT	1700	No microwave	3.88	7.32	2.61
MM	1400	Multimode	2.93	7.30	2.62
SM-100:0	1400	Single Mode 100%E:0%H	2.75	7.38	2.59
SM-60:40	1400	Single Mode 60%E:40%H	2.64	7.69	2.45
SM-30:70	1400	Single Mode 30%E:70%H	3.88	8.23	2.25

*Equivalent volume percent was calculated using calibration curves from $Y_3Al_5O_{12}/Al_2O_3$ mixed-phase powders.

Another way to consider the effect of the sintering conditions on densification is to describe the samples in terms of the relative intensity of magnetic field present during heat treatment. The microwave heating of ceramics is thought to be mainly due to the dielectric loss of the material, and hence the electric field component is thought to dominate the heating process. However, it has been suggested that at elevated temperatures, the heating mechanism of ceramics may be due to a combination of factors, including dielectric loss, eddy current, and magnetic loss [8,9]. Figure 2 shows sample density plotted as a function of the ratio of magnetic to electric field. So, for example, SM-100:0 has a ratio of zero (or 0/100) while SM-30:70 has a ratio of 2.33 (or 70/30). The multi-mode sample is assumed to have a ratio of 1. While we acknowledge that our data set is limited, our preliminary results suggest that the amount of magnetic energy present may have a significant effect on densification despite the fact that magnetic fields coupled very weakly with Al_2O_3 but strongly with Er (having unpaired electrons and hence high magnetic moment). However, more work is needed to elucidate this interaction.

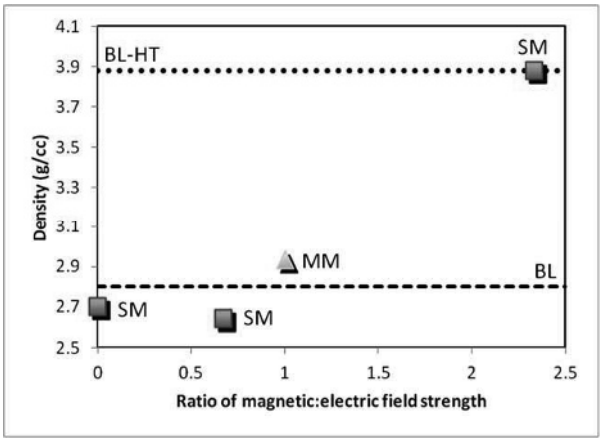

Figure 2. Ratio of magnetic to electric field strength versus density of all microwave sintered Er:Al_2O_3 with the dashed line representing the density of the conventionally sintered Er:Al_2O_3.

In order to investigate the effect of microwave parameters on Er stability and diffusion, the phase content of each sample was studied using XRD. All samples contained $Er_3Al_5O_{12}$ (ErAG) after sintering. There was no remaining $ErAlO_3$. The peak height ratios were converted to ErAG concentrations using a calibration curve generated by precise mixtures of commercial $Y_3Al_5O_{12}$ (YAG) and Al_2O_3 powders. Although this analysis is semi-quantitative, since ErAG and YAG are isostructural and Er and Y have similar mass attenuation coefficients, the approximations of volume percent should be very close between ErAG and YAG. Thus we refer to the ErAG concentrations as equivalent concentrations, and these are indicated by an asterisk in Table I.

While phase composition does not vary as widely as density across the sample set, there still appears to be an observable effect. The baseline samples at both temperatures, as well as SM-100:0 and MM, were composed of ~2.6 volume percent ErAG. This amount of second-phase ErAG corresponds to an overall Er:Al cation ratio of ~0.54%, which matches our initial concentration quite well. This indicates that all Er in these samples has been used to form second phase precipitates and that very little, if any, remains in the crystal structure. Once again, the SM-30:70 sample displays the most interesting characteristics, with an ErAG concentration of 2.25. This indicates that the 30%E:70%H microwave sintering condition was possibly the most favorable in terms of preventing Er from diffusing out of the crystal structure. If the remaining Er is still in solution within the Al_2O_3, then ~ 0.08% Er doping has been achieved.

The phase composition data is shown in Figure 3, and the equivalent volume percent of ErAG is plotted as a function of the ratio of magnetic to electric field intensity. In this plot, the preliminary results suggest that increasing the magnetic component of the microwave field decreases second phase formation. One method to validate these results is to measure Er fluorescence characteristics across the sample. This work is currently underway. It is also not possible to fully separate the densification from the phase formation. For example, while SM-30:70 has the lowest amount of second phase, this sample also spent the least amount of processing time at lower densities where surface diffusion is a viable route for mass transport. Current work is ongoing to address this issue by monitoring phase composition and/or Er fluorescence after annealing, or under different microwave conditions, of samples that are *already dense*.

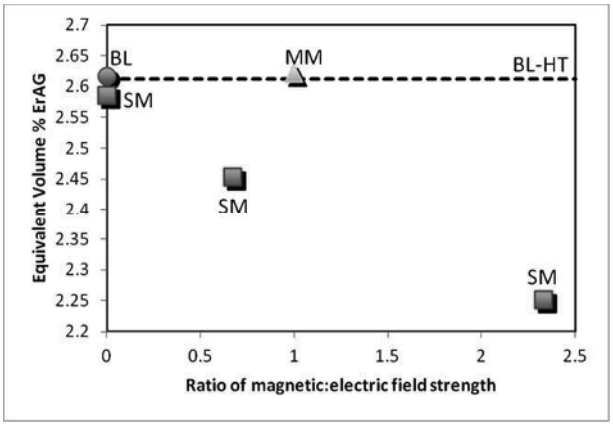

Figure 3. Ratio of magnetic to electric field versus equivalent volume percent of ErAG of all microwave sintered Er:Al_2O_3, with the dashed line representing the equivalent weight percent of the conventionally sintered Er:Al_2O_3.

The microstructure of the MM sample is shown in Figure 4. A high degree of porosity was observed, as suggested by the density results. The average grain size of the sample was ~250-300 nm, and the grain size distribution was very uniform. SEM micrographs of samples BL, SM-100:0, and SM-60:40 were all very similar to Figure 4. The microstructure of SM-30:70, however, was quite different (Figure 5). As can be seen in the secondary electron image of Figure 5a, SM-30:70 has much less porosity, which again confirms the density results. SM-30:70 also had coarser grains, up to ~1 micron on average with a somewhat bimodal character. The coarser grains can be explained by the reduction of pore drag associated with higher densities. The backscattered electron SEM image of the same sample is shown in Figure 5b, with the brighter phases reflecting a higher atomic number. The second phase bears some resemblance to amorphous secondary phases. Many of the interfaces with the Al_2O_3 grains are low-curvature/concave or high-curvature/convex, much like a pore-filling liquid phase. EDS scans (not shown) of these regions indicated that Si, the most common liquid forming impurity in Al_2O_3, was not present.

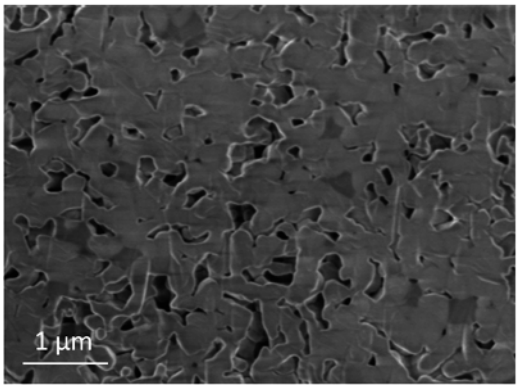

Figure 4. SEM images of sample MM using secondary electrons. A high degree of porosity can be seen in the region which was ion-polished.

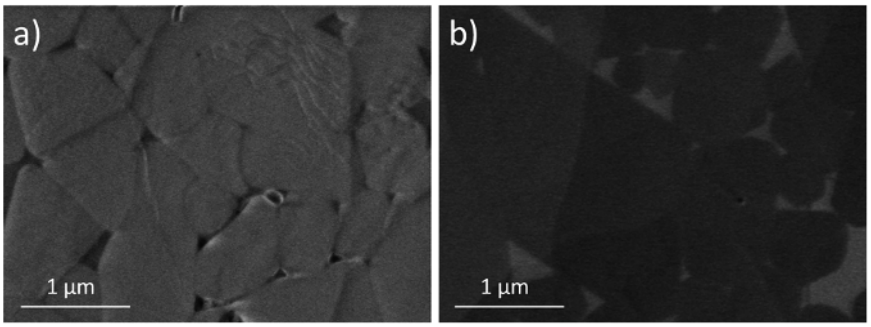

Figure 5. SEM images of sample SM-30:70 using secondary electrons (a) and back-scattered electrons (b). Regions of differing Z-contrast are very clear in (b).

SUMMARY AND CONCLUSIONS

$Er:Al_2O_3$ powders were synthesized by co-precipitation and sintered using either traditional pressure-less sintering or microwave sintering. By utilizing two different types of microwave sintering, multi-mode and single-mode, the effect of different types of microwave fields on the sintering behavior of $Er:Al_2O_3$ was studied. Using single-mode microwave sintering, the percentages of electric and magnetic fields that the sample was exposed to during sintering was varied by adjusting the position of the sample along the processing microwave cavity. This experimental parameter has not been widely explored in microwave sintering, and may provide new insight into how the different fields affect a variety of processes throughout the sintering process. Our preliminary results suggest that this may be the case.

Overall, the microwave sintering parameters appear to have a profound influence on the densification and, possibly, RE migration/phase stability. Sintering in the single-mode microwave system, with a 30%E:70%H *mixed field* produced samples with significantly higher density (~97% of theoretical of alumina) than all of the other samples sintered at 1400°C (and equal to the sample conventionally sintered at 1700°C). This high density represents a

significant improvement over the conventionally-sintered (1400°C) sample, which had a density ~70% of the theoretical density. Whether due to the higher density or a microwave effect in itself, this sample also contained the least amount of second phase, which indicated that more Er formed a solid solution with Al_2O_3. While our results indicated that densification and Er stability within the lattice may both improve with increasing magnetic field, our data is too limited to form a concrete conclusion. Regardless, our findings suggest that the magnetic component may play a critical, if not well understood, role in the processing of weakly magnetic materials such as Al_2O_3, and that the dopant material (RE in this case) may play an important role to the material response to the EM fields.

REFERENCES

1. T. Watanabe, S. Tsurekawa, X. Zhao, and L. Zuo, "Grain Boundary Engineering by Magnetic Field Application," *Scripta Materialia*, 54 (6) (2006), 969-975.
2. Y. Sakka, T. S. Suzuki, and T. Uchikoshi, "Fabrication and Some Properties of Textured Ceramics by Colloidal Processing in High Magnetic Field," *Key Eng. Mater.*, 352 (2007), 101-106.
3. R. Roy, R. Peelamedu, L. Hurtt, J. Cheng, and D. Agrawal, "Definitive Experimental Evidence for Microwave Effects: Radically New Effects of Separated E and H Fields, such as Decrystallization of Oxides in Seconds," *Mat. Res. Innovat.,* 6 (2002), 128-140.
4. Rustum Roy, Dinesh Agrawal, and Jiping Cheng, "New First Principles of Microwave-Material Interaction: Discovering the Role of the H Field and Anisothermal Reactions," in *Microwaves: Theory and Application in Materials Processing V*, (Westerville, OH: American Ceramic Society, 2001), 471.
5. J. Cheng, R. Roy and D. Agrawal, "Radically different effects on materials by separated microwave electric and magnetic fields," *Mat. Res. Innov.*, 5 (2002), 170-177.
6. S. Horii, A. Ishihara, T. Fukushima, T. Uchikoshi, H. Ogino, T.S. Suzuki, Y. Sakka, J. Shimoyama, and K. Kishio, "Magnetic Orientation and Magnetic Anisotropy in Paramagnetic Layered Oxides Containing Rare-earth Ions," *Sci. Technol. Adv. Mater.*, 10 (2009), 014604.
7. J.D. Livingston, H.R. Hart Jr., and W.P. Wolf, "Paramagnetic Anisotropy in High-T_C Superconductors," *J. Appl. Phys.*, 64 (1988), 5806-5808.
8. Noboru Yoshikawa, "Recent Studies on Fundamentals and Application of Microwave Processing of Materials," in *Advances in Induction and Microwave Heating of Mineral and Organic Materials*, (Rijeka, Croatia: InTech Europe, 2011), 3.
9. D. Agrawal, "Microwave Sintering of Ceramics, Composites, Metals, and Transparent Materials," *J. Mater. Education*, 19 (1997), 49-57.