Anisothermal reaction synthesis of garnets, ferrites, and spinels in microwave field

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Abstract

The experimental achievement of reacting two phases that are held at two different temperatures—the anisothermal reaction condition—is a radical innovation in materials chemistry. Details on the synthesis of Yttrium Iron Garnet (Y$_3$Fe$_5$O$_{12}$), Barium Ferrite (BaFe$_{12}$O$_{19}$), and Nickel Aluminate (NiAl$_2$O$_4$) in 1–10 min in a microwave field are provided. The starting precursor oxides were chosen such that they include a low and a high microwave absorbing phases. When these mixtures are exposed to a 2.45-GHz multimode microwave field the highly absorbing powder particles act as (micro)heat sources and the low absorbing powder particle act as (micro)heat sinks, and create the “anisothermal heat distribution,” a hitherto never attained phenomenon in materials science. A comparison study carried out comparing conventional reactions of the same phases suggested that the “anisothermal heating phenomenon” is also responsible for the very rapid reactions and product formations. Model experiments performed with an Y$_2$O$_3$/Fe$_3$O$_4$ diffusion couple showed a unidirectional diffusion of Fe species into Y$_2$O$_3$, forming a different sequence of intermediate phases. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

All solid-state reactions of metals, ceramics, and semiconductors carried out in conventional furnaces take place under essentially isothermal conditions. The transfer of heat from

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the external heating elements of the furnace to the constituent phases in the sample occurs by convection, radiation, and conduction. In sudden insertion of a mixed phase sample into a preheated furnace small temperature gradients must exist as thermal conductivities of the phases differ. Even such small gradients last only for seconds depending on the size and phase contents. For example, the typical heating of a cold sample placed in a cold furnace from ambient to 1500°C in a few hours will involve much smaller gradients compared to those which arise when inserting a cold pellet in a preheated furnace at 1500°C. But we show below the differences of temperatures are orders of magnitude less than what we achieve in a microwave field.

Since 1985, [1] our microwave radiation–solid matter research has produced a sequence of surprising and useful results. The extraordinary kinetics we achieve (e.g., sintering apatite to transparency in 3 min) suggest something very different about the microwave heating compared to conventional furnace heating. Certainly the generalized increase in kinetics of sintering by 10–100 times requires an explanation, especially because it has already been demonstrated in a wide variety of systems—apatite [2], alumina [3], spinel [3], WC-Co [4], metals [5], etc.

The most dramatic synthesis example in our early work [6] was in the BaCO$_3$–TiO$_{2-x}$ system, where one could get reactions in 1 min, which could not be attained in 12 h in conventional furnaces. The reaction between Si and C leading to SiC also occurs very rapidly, at much lower temperatures compared to conventional reactions, where C shows very high microwave susceptibility in a 2.45 GHz, multimode microwave oven [7]. Similar ultrarapid microwave syntheses of various compounds have been reported by many other researchers world wide [8–11], notably Shimada et al. in the Y$_2$O$_3$–Fe$_2$O$_3$ system in a 28-GHz field.

Very recently Roy et al. [12] proposed that this anisothermal condition was one aspect of the elusive “microwave effects” in material exposure to microwaves at least in two (or more) component systems. It was claimed that microwave–material interaction develops a reaction condition for a prolonged period, of a hitherto never attained condition in materials science—“anisothermal reactions”. As the term implies, this means two intimately mixed solid phases react while one is maintained at a much higher temperature than the other. This phenomenon is illustrated in Fig. 1. Of course, this is a continuously changing condition as the reaction proceeds. To date, computer searches have found no information in the literature on such “anisothermal reactions” and associated reaction or diffusion mechanisms.

In the present experiments, we have chosen few two-phase systems in which the microwave absorptivities of the two powders are very different from each other. The larger their absorptivity difference, the higher the “anisothermicity” of the reaction. A large temperature difference could well lead to a different reaction path, and hence, different intermediate phases, and involve diffusion paths different from those in conventional isothermal heating. In this communication, we report on a study comparing isothermal and anisothermal reactions in powder mixtures of Y$_2$O$_3$+$\text{Fe}_2\text{O}_4$, BaCO$_3$+$\text{Fe}_3\text{O}_4$, and NiO+$\text{Al}_2\text{O}_3$. Model experiments were also carried out to understand the direction of diffusing species in such anisothermal powder reactions.
analysis (EDAX) attached to the SEM. X-ray mapping procedures were utilized to determine composition distributions during the reactions.

3. Results and discussion

3.1. Powder reactions

3.1.1. \( Y_2O_3-Fe_3O_4 \) system

The time temperature graph for \( Fe_3O_4 \) and \( Y_2O_3/Fe_3O_4 \) powder mixtures are shown in Fig. 2. Pure \( Y_2O_3 \) powder did not show any microwave absorption behavior until 1000°C (not shown in Fig. 2). It is interesting to compare the difference in heating behaviors of pure \( Fe_3O_4 \) and \( Y_2O_3/Fe_3O_4 \) powder mixture. Up to 600°C the pure \( Fe_3O_4 \) heating rate was faster than the powder mixture’s, whereas beyond this temperature the powder mixture had a faster rate than pure \( Fe_3O_4 \). An intermediate product formation and its superior absorption behavior are believed to be responsible for this trend. The choice of \( Fe_3O_4 \) as the source of iron is due to the fact that the absorptivity of \( Fe_2O_3 \) at 2.45 GHz is very low. In an earlier note [15] we showed that although Kimura et al. used \( Fe_2O_3 \) in a similar study, they were working at 28 GHz.

Powder reactions were carried out by keeping the temperature constant and by varying the reaction time. Similarly, reactions were also carried out by maintaining the reaction time
constant and varying the reaction temperature. Reactions were also carried out in different atmospheres, namely air and nitrogen. X-ray diffractograms corresponding to the temperature-dependent reactions are shown in Figs. 3 and 4. Referring to Fig. 3, it can easily be seen that almost pure Y₃Fe₅O₁₂ (YIG) is formed in 5 min at 1300°C. Microwave synthesis of YIG has been accomplished previously in a single mode by other workers [16,17]. In our samples, YFeO₃ also exists to a minor extent after 10 min of reaction. When the same reaction was carried out in pure nitrogen, only the YFeO₃ phase formed. Formations of YIG in air and YFeO₃ in nitrogen clearly elucidate the high-temperature chemical stability of these compounds in various environments. The morphological features (Figs. 5 and 6) of microwave-synthesized Y₃Fe₅O₁₂ and YFeO₃ did not reveal any significant differences. In general, it can be said that YFeO₃ grains were relatively bigger compared to YIG grains. At a constant temperature of 1300°C, time-dependent reactions were carried out in air. Corresponding XRD patterns are shown in Fig. 7. Almost phase-pure YIG has been formed roughly in 10 min. Time-dependent reactions also proved that YIG particles grow at the expense of YFeO₃ particles.

3.1.2. BaCO₃-Fe₃O₄ system

In YIG formation reactions the ratio in the mixture of Y₂O₃ and Fe₃O₄ is 3:5, while it is 1:4 in BaFe₁₂O₁₉ formation reactions. This means the concentration of “heat sources” is
Fig. 4. XRD patterns of a $\text{Y}_2\text{O}_3$–$\text{Fe}_3\text{O}_4$ mixture microwave heated to different temperatures for a constant duration of 5 min in pure nitrogen.

relatively high in the $\text{BaO}/4\text{Fe}_3\text{O}_4$ composition compared to the $\text{Y}_2\text{O}_3$/Fe$_3$O$_4$ mixture. This may lead to a much more effective (faster) heating in the $\text{BaO}/4\text{Fe}_3\text{O}_4$ case. A comparison study was carried out for samples reacted at 800°C in conventional and microwave furnaces. The microwave reacted samples were relatively darker in color compared to the conventional ones, indicating that the microwave samples had reacted to a greater extent. The XRD patterns of conventionally and microwave reacted samples are shown in Fig. 8a and b, respectively. In the case of conventional reactions (Fig. 8a) after 2 min of dwell time at 800°C, no transformation to BaFe$_{12}$O$_{19}$ had occurred. Major peaks corresponded only to the unreacted BaCO$_3$ and Fe$_2$O$_3$. Indeed, no great difference was observed by increasing the dwell time from 2 to 10 min. On the other hand, after 2 min (in the case of microwave-reacted sample), more than 70% formation of BaFe$_{12}$O$_{19}$ was observed. Complete conversion to BaFe$_{12}$O$_{19}$ was achieved at 900°C in just 5 min. The microstructure of barium ferrite (BaFe$_{12}$O$_{19}$) prepared by microwave at 1100°C in 5 min showed well-faceted, platelet microstructure (Fig. 9). The particle morphology indicates sufficient diffusion (supported by XRD) that had led to the complete formation of reaction product, in the form of platelets.
3.1.3. NiO–Al₂O₃ system

The NiO–Al₂O₃ system was investigated for anisothermal reactions, as one in which NiO absorbs microwaves very strongly beyond 400°C whereas, Al₂O₃ does not absorb microwaves even beyond 1200°C. This makes NiO–Al₂O₃ a good model for anisothermal reaction system. The details of microwave absorption experiments and corresponding t-T graph can be found elsewhere [18]. The X-ray diffractograms of microwave and conventionally prepared products are shown in Fig. 10a and b. It was calculated that at 1200°C about 90% NiAl₂O₄ is formed in the case of (amisothermal) microwave reaction for 15 min, whereas, this value is <30% in the case of conventional, isothermal reaction after 20 min. At 1400°C, the NiO+Al₂O₃ mixture was completely transformed to NiAl₂O₄ under microwave radiation, and in almost identical reaction conditions, in the conventional method it has transformed only to <80%. These results clearly prove again that the microwave reactions in the case of NiO–Al₂O₃ is much faster than the conventional reactions. With respect to sintering, it was observed that almost 100% density is achieved in a microwave furnace at 1300 and 1400°C, and these density values correspond only to pure NiAl₂O₄. However, in the case of conventional sintering, despite poor density, the values exceed the theoretical density value of NiAl₂O₄, clearly indicating that the samples contain other phases (see Fig. 10), as confirmed by XRD results also. The morphology of the samples sintered both by microwave and conventional methods is shown in Fig. 11a and b, respectively. The high degree of

Fig. 5. Scanning electron micrograph (SEM) of Y₃Fe₅O₁₂ (YIG) formed in microwave reactions carried out in air.
sintering observed in the case of microwave heating is visible in Fig. 11a. Grains are almost uniformly shaped and in contact with each other, suggesting that in the case of NiAl$_2$O$_4$, microwaves offer uniform sintering. The morphology of the fracture surface of the same sample is given as inset in Fig. 10a. Some amount of closed porosity is seen. The microstructure of the conventionally prepared NiO+Al$_2$O$_3$ sample reacted at 1400°C for 20 min is shown in Fig. 11b. Although the reaction conditions are similar to the microwave-sintered sample, the sample is only partially sintered with a loose particle cloud (including probably NiO, Al$_2$O$_3$ and NiAl$_2$O$_4$) distributed over the surface.

3.2. Model experiments in Y$_2$O$_3$-Fe$_3$O$_4$ system and its extrapolation to powder reactions

To understand the microwave-induced anisothermal reactions, model experiments were carried out to observe the diffusion direction of species. For model experiments, a Fe$_3$O$_4$ (highly absorptive at 2.45 GHz frequency at room temperature) pellet was placed over and in contact with the above Y$_2$O$_3$ (poor absorber of microwaves at room temperature) pellet. The sample assembly was placed at the center of a microwave tube furnace. When the microwave power is on, only the Fe$_3$O$_4$ pellet is heated and Y$_2$O$_3$ remains without any self-heating. The temperature of each pellet is measured separately. Y$_2$O$_3$ was always at a much lower temperature than Fe$_3$O$_4$, but obviously influenced by the Fe$_3$O$_4$ temperature. When these pellets were heated separately, the Y$_2$O$_3$ pellet did not show any absorption untill
1200°C, which clearly means that the temperature of the Y₂O₃ in the paired samples are due to transfer of heat by conduction and radiation mechanisms from the top Fe₃O₄ pellet. Fig. 12 shows the photograph of the Y₂O₃/Fe₃O₄ sample assembly at various stages of the

**Conventional**

\[ T=800°C \]

\[
\begin{array}{c}
\text{Intensity (arb. units)}
\end{array}
\]

\[
\begin{array}{c}
\text{Two Theta (deg.)}
\end{array}
\]

**Microwave**

\[ T=800°C \]

\[
\begin{array}{c}
\text{Intensity (arb. units)}
\end{array}
\]

\[
\begin{array}{c}
\text{Two Theta (deg.)}
\end{array}
\]

Fig. 8. XRD patterns of Barium Ferrite formation reactions in both (a) conventional (isothermal) and (b) microwave (anisothermal) reactions.
MW, 1200°C, 5 min.

Fig. 9. Platelet microstructure of pure BaFe<sub>12</sub>O<sub>19</sub> prepared in anisothermal reactions at a temperature of 1200°C in just 5 min.

**Microwave**

(15 min.)

- Al<sub>2</sub>O<sub>3</sub>
- NiO
- NaAl<sub>12</sub>O<sub>19</sub>

**Conventional**

(20 min.)

Fig. 10. XRD patterns of Nickel Aluminate formation reactions in both (a) conventional (isothermal) and (b) microwave (anisothermal) reactions.
Fig. 11. Product morphology of NiAl₂O₄ samples prepared using both (a) microwave and (b) conventional procedures. It is proven that anisothermal reactions involve rapid diffusion of species leading to fast sintering. Fracture surface micrograph is included as an inset to Fig. 7a.
Fig. 12. Model experiments showing the absorptivity differences between Fe$_3$O$_4$ and Y$_2$O$_3$ and progressive heating with microwave power. It is believed a similar heating behavior exists in a powder mixture, where Fe$_3$O$_4$ acts as a source and Y$_2$O$_3$ acts as a sink.

experiment. Diffusion experiments were carried out at 1300°C and at three different reaction times, namely 25, 60, and 90 min. The formation of a product layer was observed on the top of the Y$_2$O$_3$ layer, and increase in the layer thickness with time was also observed. After 90 min in the microwave field the top pellet shrunk due to sintering and the dimensions of the bottom pellet remain unchanged. The sintered top pellet's bottom layer was uncontaminated. Energy dispersive X-ray Analysis (EDAX) was carried out over the bottom surface of the top pellet (BTP) and top surface of the bottom pellet (TSBP). The BSTP surface showed peaks corresponding only to Fe. No Y peaks were observed (Fig. 13). However, the TSBP surface showed peaks corresponding to both Y and Fe. This clearly shows that Fe$^{3+}$ ions have diffused from a top high-temperature pellet of Fe$_3$O$_4$ to a bottom low-temperature pellet of Y$_2$O$_3$ through the interface, and no counterdiffusion of Y$^{3+}$ has taken place into the Fe$_3$O$_4$, forming an intermediate product layer. The XRD pattern of the top of the bottom pellet showed the coexistence of a mixture of YIG and YFeO$_3$ phases mixed with Y$_2$O$_3$. The surface morphology of this thin film is shown in Fig. 14, which resembled more like the one shown in Figs. 4 or 5 (YIG and YFeO$_3$). EDX patterns again confirm the presence of both Y and Fe compounds. The microstructure of BSTP was unique, showing large and well-connected grains of Fe$_3$O$_4$. This model experiment, though crude, established the fact that the anisothermal reactions in the Y$_2$O$_3$–Fe$_3$O$_4$ system involve a predominant one-directional diffusion compared to a mutual diffusion that generally takes place in conventional, isother-
Fig. 13. EDAX experiment was carried out on both bottom surface of the top pellet (BSTP) and top surface of the bottom pellet (TSBP) of a 90-min reacted diffusion couple.

...mal reactions. We feel that this "anisothermicity factor" exists inherently in many ceramic powder reactions carried out in multimode microwave furnaces. It is probably the major driving force for rapidity of the reactions in all systems with 3d and 4f elements.

A powder mixture system in a microwave field, consisting of high- and low-absorbing particles, can be considered as a randomly distributed infinite number of heat sources and heat sinks. The experiments above establish the fact that the high-temperature species readily diffuse into the low-temperature particles initially to form a thin product layer within seconds. Subsequent advancement of the reaction layer to complete conversion depends on various factors such as mol ratio of heat sources ($m_1$) to heat sinks ($m_s$), the microwave absorption of the product layer, reactant particle surface area, etc. It is logical to assume that $m_1/m_s > 1$, then the reaction proceeds rapidly, which is partly the reason for rapid reaction observed in all the above three examples. The reaction rate is going to be even more rapid if the product formed is a strong microwave absorber (as has been observed in SiC and BaFe$_{12}$O$_{15}$ formations). The schematic representation of product formation in anisothermal reactions is depicted in Fig. 15.

The evidence of incomplete reaction in the case of isothermal reactions and a more complete reaction in the case of anisothermal reactions has been examined using X-ray mapping, and is shown in Fig. 16. In this case, we examine BaCO$_3$ + Fe$_3$O$_4$ reacted under identical conditions in both conventional and microwave facilities. X-ray mapping showed a barium segregated region and iron segregated regions clearly separated from each other in
the case of isothermal reactions but stay together in microwave reacted samples. The separated region observed in the case of conventional reactions is due to unreacted particles, as supported by XRD results. They become totally miscible when they react and form BaFe$_{12}$O$_{19}$ in the case of microwave-reacted samples.

Unlike the parabolic diffusion couple, the powder reactions seem to follow a complex equation, as suggested by Carter [19]. For a conventional powder reaction, the equation (in the case of YIG formation) can be expressed as

$$\left[1 + (z - 1)\xi\right]^{2\gamma} + (z - 1)(1 - \xi)^{2\gamma} = z + 2(1 - z)\frac{kt}{r^2}$$

where $\xi$ is the relative amount of Y$_2$O$_3$ transformed into product, $r_\gamma$ is the original radius of yttria particles, $z$ is the volume of the reaction product. A mere solid-state reaction involves diffusion of various charged species across the phase boundary within the system. As explained earlier, this would only lead to parabolic behavior, where the material transformation does not occur beyond a point and the reaction remains incomplete. Hence, most of the powder reactions are believed to be a combination of a solid-state and a rapid surface diffusion or a gas-solid reaction. In rapid surface diffusion, particles open up their surfaces and there is a continuous supply of atoms to the reaction site. The above equation might still be valid for microwave-induced anisothermal solid-state reactions. Apart from the aniso-
Anisothermal powder Heating

Fig. 15. Schematic representation of a possible mode of product formation in anisothermal powder reactions.

thermal effect, the contribution for the multifold enhancement of reaction rate can also arise from electromagnetic field distribution around the source and sink particles. The electromagnetic field may assist by rapid surface opening up of particles followed by rapid interdiffusion of species and thus acts as an additional driving force for powder reactions. However, it is clearly established that the major reaction rate enhancement is due to the unique “anisothermal” conditions that drive the directional diffusion as proved by the model experiment.

4. Conclusions

Anisothermal heating is a completely new phenomenon in ceramics. In this paper, it has been demonstrated in several different systems. Anisothermic reactions are always very fast compared to conventional, isothermal solid-state reactions. This has been demonstrated in various systems like $Y_2O_3$–$Fe_3O_4$, $BaCO_3$–$Fe_3O_4$, and $NiO$–$Al_2O_3$. In all these systems, one compound is a good microwave absorber, and the other is not, creating the unique “aniso-
Fig. 16. X-ray maps of BaCO$_3$ + Fe$_3$O$_4$ mixture reacted for identical conditions for both conventional and microwave reactions.

thermal environment within the system. Our model experiments clearly establish the fact that the hotter species diffuse rapidly into the relatively colder ones. This has led to intermediate products with different stoichiometry compared to the stoichiometry of the products obtained in isothermal reactions. Also, in microwave reactions the Y$_3$Fe$_5$O$_{12}$, BaFe$_{12}$O$_{19}$, and NiAl$_2$O$_4$ products were obtained in much shorter times compared to