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Synthesis of Inorganic Materials by 28 GHz Microwave Irradiation

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Various inorganic materials have been successfully synthesized by 28 GHz microwave irradiation. When a material absorbs microwaves well, the material can be heated through microwave-material interactions. The interactions are identified as energy losses in the material, resulting in rapid volumetric heating. Microwave absorption behavior of various inorganic materials was analyzed by measuring the temperature-time profiles under microwave irradiation. It is concluded that the temperature rise of a material under microwave irradiation is mostly attributed to the induction loss caused by electric conduction. The current topics of microwave processing achieved in our laboratory are presented in this paper. In some cases, unexpected products can be obtained *via* microwave processing.

Key words: Microwave processing, Transition metal oxides, Grain growth, Solid state diffusion

1. INTRODUCTION

Microwave processing of ceramic materials is one of the attractive fields in recent materials science. The processing has been applied for sintering and joining of various ceramic components, and more recently been applied for synthesizing various inorganic materials. Many researchers gave evidences of enhancing solid state reaction rate or diffusion rate under microwave dielectric field [1-5].

If some constituent materials in a chemical reaction system strongly absorb microwaves, the resulting heat generation can be used to drive a reaction with other components. One of the potential advantages of microwave synthesis is reduction of reaction time and temperature due to an enhancement of diffusion rate. Such an enhancement is possibly caused by material-microwave interactions; however, the effect of electromagnetic field on solid state diffusion is still not clear. The interactions are identified as energy losses in the material, generally induced by dielectric polarization, electric conduction, and/or possibly magnetic resonance. These energy losses cause a volumetric heating within a material.

Multi-mode microwave heating system operated at a frequency of 2.45 GHz (λ=122 mm) is widely used such as microwave oven, but it has a problem in uniformity of microwave electromagnetic field due to its relatively long wavelength. A multi-mode 28 GHz (λ=10.7 mm) microwave heating system can achieve a uniform electric field distribution as compared to 2.45 GHz system. We have recently demonstrated that the use of 28 GHz microwaves is effective in synthesizing various inorganic materials [6-15].

Since the chemical reaction under microwave, electromagnetic field is strongly affected by material-microwave interactions, it is very important to know the microwave absorption behavior of materials in order to utilize the microwave energy for various ceramic processing. In this paper, the current topics of microwave synthesis achieved so far in our laboratory are presented.

2. 28 GHz MICROWAVE HEATING SYSTEM

Multi-mode microwave heating system operating at a frequency of 28 GHz (Model FMS-10-28, Fuji Dempa Kogyo Co., Ltd., Japan) is used in our laboratory for the synthesis of various inorganic materials. Figure 1 shows an overview of the microwave processing equipment with a 28 GHz gyrotron generator. The

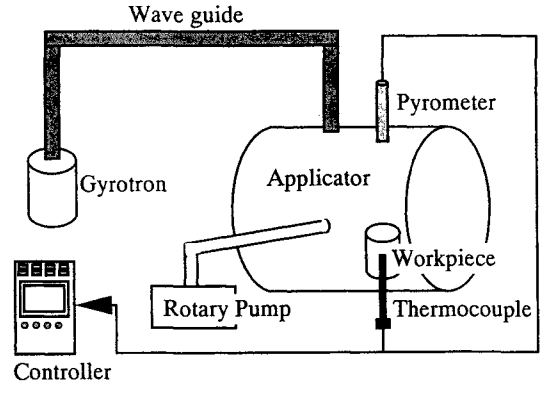

Fig. 1 General scheme of the multimode 28 GHz microwave processing equipment.

maximum power output is 10 kW.

For typical synthetic experiment, powder and/or pellet specimen is placed in a quartz tube with quartz glass wool as a heat insulating material. Quartz can be used as a crucible and thermal insulating material for microwave processing because SiO_2 is transparent to 28 GHz microwaves. The quartz tube is set in the microwave applicator (chamber), 0.7 m in diameter and 1 m in depth. The temperature of the specimen is monitored during microwave irradiation by a Pt-Pt/10%Rh thermocouple that is directly inserted into the specimen. A platinum sheath with a diameter of 1.5 mm is used to achieve an effective shielding from the microwave field. Detailed descriptions of the experimental setup are given in our previous papers [7, 8].

3. MICROWAVE ABSORPTION BEHAVIOR

When a material absorbs microwaves well, the material can be heated through microwave-material interactions. The interactions are identified as energy losses in the material, resulting in volumetric heating. The degree of microwave-material interaction (coupling), *i.e.*, the microwave absorption efficiency of a material, can be well demonstrated in the temperature-time profile of the material during microwave irradiation.

Figure 2 shows the typical temperature-time profiles of materials under microwave irradiation. The curves (a) and (b) represent the cases for strong material-microwave coupling and the curve (c) shows a moderate coupling. For a material which is transparent to microwaves or which reflects microwaves, the profile appears to be the curve (d). As reviewed by Mingos *et al.* [2], many transition metal oxides absorb 2.45 GHz-microwaves well, while there are few reports on the degree of microwave absorption for various inorganic materials at higher frequency.

The degree of microwave absorption of various inorganic materials was evaluated from the temperature-time profile under microwave irradiation at 1 kW power output. Figure 3, for example, shows temperature-time profiles of p-block oxides during 28 GHz microwave irradiation. Both In_2O_3 and SnO_2 absorb microwaves strongly, and can be heated rapidly above 800°C within

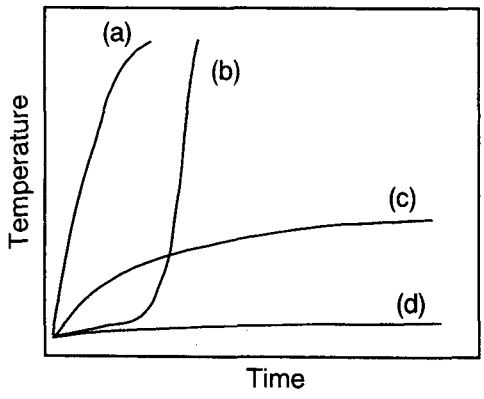

Fig. 2 Typical temperature-time profiles of materials during microwave irradiation. Curves (a) and (b) show strong microwave-material coupling, (c) moderate, and (d) weak.

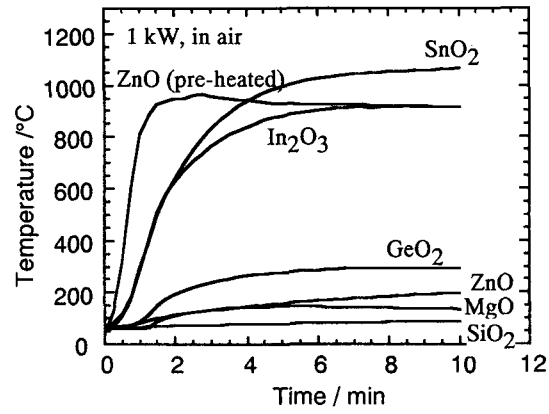

Fig. 3 Temperature-time profiles of p-block oxides during 28 GHz microwave irradiation.

5 min. GeO_2 and ZnO show moderate coupling with microwaves, while MgO weak. SiO_2 is transparent to microwaves. Considering the fact that In_2O_3 and SnO_2 are non-stoichiometric semiconductors having high electrical conductivity, material-microwave coupling in both compounds possibly correlates with higher concentration of conduction electrons. It is noted that ZnO preheated at high temperature shows strong coupling with microwaves. This is obviously due to the increase of carrier concentration induced by defect formation.

Similarly, the temperature-time profiles were measured for transition metal oxides, rare-earth metal oxides, semiconducting non-oxides, and metal powders. Generally, transition metal oxides absorb microwave energy well and are easily heated above 600°C within 2 min. Semiconducting non-oxides, *e.g.*, Si, Ge, beta-B, and SiC, also show strong coupling with microwaves (corresponding to curve (a) in Fig. 2). On the other hand, most of rare-earth metal oxides do not absorb microwaves. Exceptions are Tb_4O_7 and CeO_2. It is noted that both compounds exhibit electrical and ionic conductivity attributed to oxygen non-stoichiometry.

In summary of this section, the temperature rise of a material (caused by microwave-material interaction) is mostly attributed to the induction loss caused by electric conduction.

4. SYNTHESIS OF INORGANIC MATERIALS

4.1 Complex oxides

Amorphous ferrites: The powder mixture of MO (M= Ni, Co, Zn) and α-Fe_2O_3 to form spinel composition (MFe_2O_4) was irradiated at 2.0-4.0 kW microwave power (28 GHz). The temperature of the mixture gradually increased and began to rise rapidly at a certain point (see the curve (b) in Fig. 2). The threshold points were *ca.* 160°C for M=Ni, 300°C for M=Co, and 400°C for M=Zn. Over the point, the temperature reached 1400°C within a minute for all cases. Microwave irradiation was stopped immediately after the temperature reached 1400°C. After irradiation, the specimen turned glossy black, indicating a rapid formation of a compound. The product has no diffraction peaks for X-ray, indicating an amorphous

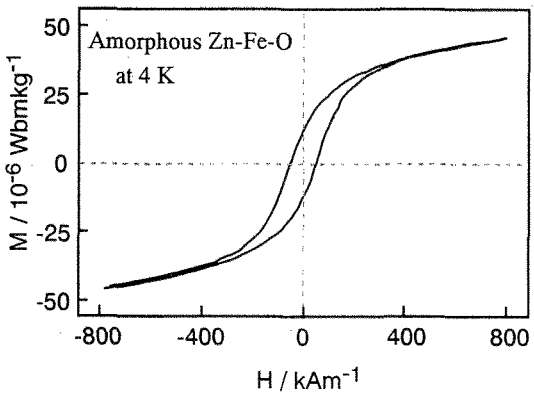

Fig. 4 Magnetic field dependence of magnetization of amorphous Zn-Fe oxide obtained by microwave irradiation.

nature of the product. Surprisingly, this amorphous phase did not crystallize by heat treatment up to 1200°C, but easily crystallized into corresponding spinel phase by applying shear stress using an alumina mortar and pestle [10]. The amorphous phases of $NiFe_2O_4$ and $CoFe_2O_4$ have similar magnetic properties to their crystalline spinel phases, but their coercive forces (H_c) are much smaller than those of the crystalline phases. The most striking difference between amorphous and crystalline phases is found in the case of $ZnFe_2O_4$. Figure 4 shows the magnetic field dependence of magnetization of microwave-processed amorphous $ZnFe_2O_4$. As seen in the figure, the amorphous $ZnFe_2O_4$ behaves like a ferromagnet, although the crystalline $ZnFe_2O_4$ is antiferromagnet.

The above results give an evidence of importance of the magnetic field in microwave processing. The importance of the magnetic field has also been pointed out by a group of MRL at Penn State [16, 17], stating that the role of the magnetic field is a major factor in all microwave heating.

$LaCrO_3$: Synthesis of perovskite-type $LaCrO_3$ generally requires high-temperature (>1000°C) heat treatment. The strong coupling of Cr_2O_3 with 28 GHz microwaves can be used to accelerate the reaction with La_2O_3 to form $LaCrO_3$. Powder mixture of Cr_2O_3 and La_2O_3 was heated to 420°C by microwave irradiation of 0.3 kW power. After 15 min-irradiation, single phase $LaCrO_3$ was obtained. It is surprising that the reaction proceeded within a short period even at such a low temperature. Moreover, scanning electron microscopy (SEM) observation revealed a considerable grain growth within the product [7]. This result suggests a drastic enhancement of the diffusion rate. Such an enhancement of grain growth process is also found in microwave-processed $Na_x(Co,Mn)O_2$ [11] and $(In_{0.67}Fe_{0.33})_2O_3$ [12].

4.2 Non-oxides

Microwave energy can also be used for the processing of non-oxide materials. As mentioned in section 3, semiconducting non-oxides (Si, Ge, and beta-B) can be heated by microwave irradiation, indicating possible synthesis of silicides, germanides, and borides of various metals. In addition, we found that metal powders (not bulk specimen) could be heated to moderate temperature (400-800°C) without sparking in the microwave chamber. In this section, examples of microwave synthesis of non-oxides are given.

Metal-doped β-B: Beta-rhombohedral boron strongly absorbs 28 GHz microwaves and can be heated to a temperature of 1500°C within 4 min. Using this strong coupling, iron-doped β-B with various dopant concentrations (B/Fe=30-45) were successfully synthesized in a short time by microwave irradiation. Figure 5 shows the X-ray diffraction pattern of B/Fe=30 specimen after 10 min-irradiation at 3.0 kW along with the diffraction pattern of β-B itself. The diffraction intensities of the microwave-processed specimen drastically changed from those of β-B, although the peak positions remained unchanged. This result is an evidence of successful incorporation of iron into the β-B lattice. The Rietveld refinement and the electrical conductivity measurements supported the fact that Fe-doped β-B was successfully synthesized by microwave irradiation [14].

The SEM photograph of the microwave-processed Fe-doped β-B is shown in Fig. 6. Particle size and morphology of the microwave-processed specimen are nearly the same as starting β-B powder. This situation is opposite to the cases of $LaCrO_3$ and many other oxides (see section 4.1). Such difference might be caused by a difference in penetration depth of microwave energy within materials. The lack of grain growth in the microwave-processed boron compound may be attributed to relatively shallower penetration depth due to its high electrical conductivity (skin effect).

Transition metal nitrides: Microwave processing sometimes yields an unexpected product. Transition metal powder was heated to 400-800°C by microwave irradiation. In the cases of Ti, Cr, and Mn, formation of nitrides was confirmed after irradiation in air. Surprisingly, metal oxides did not formed [15, 18]. Grain size of the obtained nitrides was just the same as

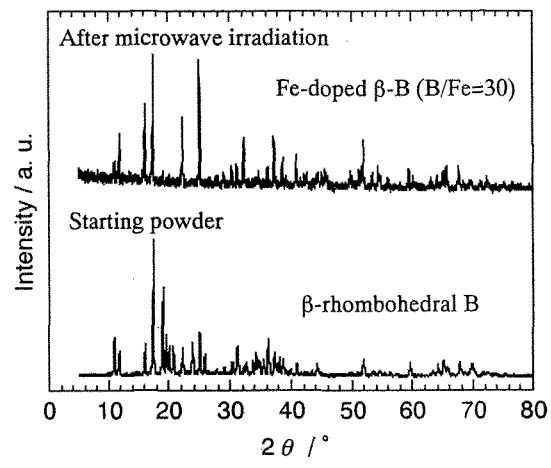

Fig. 5 X-ray diffraction patterns of β-rhombohedral boron and Fe-doped β-boron (B/Fe=30) synthesized by microwave irradiation.

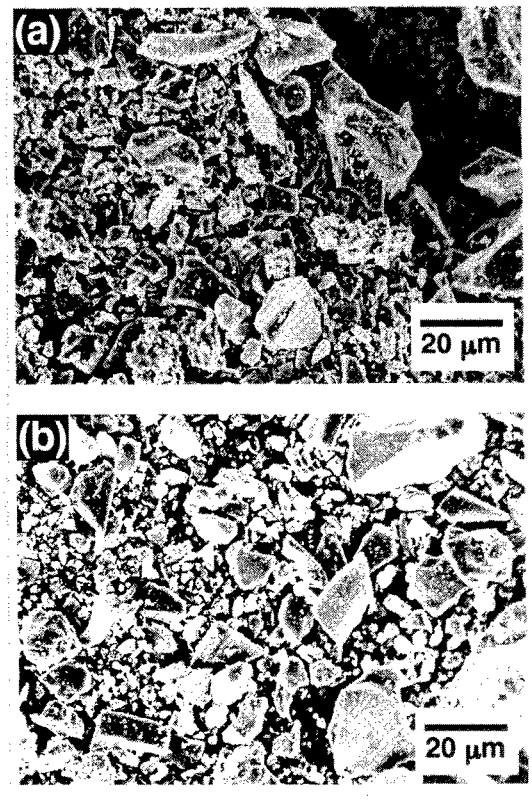

Fig. 6 SEM photgraphs of (a) starting β-B powder and (b) microwave-processed Fe-doped β-B.

that of the starting metal powder, suggesting an interstitial mechanism of formation. The degree of nitride formation is strongly dependent on the particle size of the starting metal powder. Nitrides were formed at the surface of metal particles and the thickness of nitride layer was limited to a certain amount. Prolonged microwave irradiation did not accomplish further nitridation, suggesting an importance of microwave penetration depth on the formation of nitrides. In fact, the thickness of nitride layer is in good agreement with the estimated penetration depth (δ=1-2 μm) using the following equation [19]:

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} \qquad (1)$$

where f is a frequency of microwave, and μ and σ are the magnetic permeability and the electrical conductivity of the material.

5. CONCLUSION

We have demonstrated that the use of 28 GHz microwave energy is effective in synthesizing inorganic materials containing microwave-susceptible components. The volumetric heating due to absorption of microwave energy within a material is mainly caused *via* conduction mechanism rather than dielectric loss mechanism. In addition, the magnetic field plays an essential role on the microwave processing of a material. In conclusion, microwave processing is an attractive method in material synthesis because of the possible unequibrium nature originated in microwave-material coupling, as well as rapid internal heating.

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REFERENCES

[1] W. H. Sutton, Am. Ceram. Soc. Bull., **68** 376-86 (1989).
[2] D. M. P. Mingos and D. R. Baghurst, Chem. Soc. Rev., **20**, 1-47 (1991).
[3] J. H. Booske, R. F. Cooper, and S. A. Freeman, Mater. Res. Innov., **1**, 77-84 (1997).
[4] J. Jacob, L. H. L. Chia, and F. Y. C. Boey, J. Mater. Sci., **30**, 5321-27 (1995).
[5] R. Roy, D. Agrawal, J. P. Chen, and M. Mathis, in "Microwave: Theory and Application in Material Processing IV", Edited by D. E. Clark, W. H. Sutton, and D. A. Lewis, Ceramic Transactions, **80**, The American Ceramic Society, Westerville, (1997) pp. 3-26.
[6] T. Kimura, H. Takizawa, K. Uheda, T. Endo, and M. Shimada, J. Am. Ceram. Soc., **81**, 2961-64 (1998).
[7] M. Iwasaki, H. Takizawa, K. Uheda, T. Endo, and M. Shimada, J. Mater. Chem., **8**, 2765-68 (1998).
[8] M. Iwasaki, H. Takizawa, K. Uheda, and T. Endo, J. Jpn. Soc. Powder & Powder Metallurgy, **47**, 999-1003 (2000). [in Japanese]
[9] T. Kimura, H. Takizawa, K. Uheda, T. Endo, and M. Shimada, J. Mater. Synth. Proc., **9**, 57-61 (2001).
[10] T. Kimura, H. Takizawa, K. Uheda, and T. Endo, Proceedings of the 2nd International Conference on Microwave Chemistry, (Ampere Antibes 2000), 335-338 (2000).
[11] M. Iwasaki, H. Takizawa, K. Uheda, and T. Endo, J. Mater. Sci. Lett., **19**, 2033-35 (2000).
[12] H. Takizawa, K. Uheda, and T. Endo, J. Am. Ceram. Soc., **83**, 2321-23 (2000).
[13] H. Takizawa, K. Uheda, and T. Endo, J. Mater. Sci. Lett., **20**, 359-61 (2001).
[14] H. Takizawa, N. Haze, K. Okamoto, K. Uheda, and T. Endo, Mater. Res. Bull., (2002) in press.
[15] T. Kimura, H. Takizawa, K. Uheda, and T. Endo, J. Jpn. Soc. Powder & Powder Metallurgy, **46**, 378-382 (1999).
[16] R. Roy, D. Agrawal, and J. P. Cheng, in " Micorwave: Theory and Application in Material Processing V", Edited by D. E. Clark, Jon G. P. Binner, and D. A. Lewis, Ceramic Transactions, **111**, The American Ceramic Society, Westerville, 2001.pp. 471-85.
[17] R. D. Peelamedu, R. Roy, and D. Agrawal, Mater. Res. Bull., **36**, 2723-2739 (2001).
[18] manuscript in preparation.
[19] K. Kato, K. Takahashi, H. Mitera, and K. Minami, Jpn. J. Appl. Phys., **27**, 1641 (1988).

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