# Preparation of Mesoscopic $TiO_2$–$SnO_2$ Composite Grains by Spinodal Decomposition under 28 GHz Microwave Irradiation

Hirotsugu Takizawa,* Akio Hagiya, Takuya Aoyagi, and Yamato Hayashi
*Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai 980-8579*

(Received April 24, 2008; CL-080428; E-mail: takizawa@aim.che.tohoku.ac.jp)

$TiO_2$–$SnO_2$ composite with the modulated lamellar structure was obtained within a short period by microwave irradiation using 28-GHz frequency. Single-phase solid solution with the rutile-type structure was formed at the early stage of irradiation, and the prolonged irradiation caused the formation of mesoscopic lamellar structure induced by spinodal decomposition. Such a nonequilibrium nature is believed to be due to selective heating behavior under microwave irradiation.

Microwave heating is rapidly becoming an established procedure for inorganic and organic synthesis. If a material couples with microwaves, the material can be heated via material–microwave interaction. The resultant heat can be used to drive a chemical reaction with other components.[1] In microwave processing, we can find many benefits, especially, short processing time because of enhancement of diffusion rate. Such an enhancement is believed to be due to microwave effects consisting of "thermal" and "nonthermal" effects. Thermal effect includes rapid, internal, and selective heating. Nonthermal effect is possibly caused by material–microwave interaction; however, the effect of electromagnetic field on solid-state diffusion is still not clear.

Microwave heating system operated at a frequency of 2.45 GHz is widely used in such applications as microwave oven, but it has a problem in uniformity of microwave dielectric field due to its relatively long wavelength ($\lambda = 122$ mm). A multimode 28 GHz ($\lambda = 10.7$ mm) microwave heating system can achieve more uniform electric field distribution. We have recently demonstrated that the use of 28 GHz microwaves is effective in synthesizing various inorganic solid materials.[2–6]

The binary $TiO_2$–$SnO_2$ system is well known to exhibit a miscibility gap at low temperature, showing spinodal decomposition in the temperature range 800–1400 °C.[7] This binary system is a typical selective heating system under microwave irradiation because $SnO_2$ strongly couples with microwave energy, whereas $TiO_2$ does not. In such a case, solid-state diffusion mechanism of each species under microwave electromagnetic field would much differ from that in conventional heating. This may cause a nonequilibrium nature of microwave-processed specimen.

Powders of $TiO_2$, $SnO_2$, and $\alpha$-$Al_2O_3$ were used as starting materials. Addition of a small amount of $\alpha$-$Al_2O_3$ was effective in facilitating the spinodal decomposition.[8] Equimolar amounts of $TiO_2$ and $SnO_2$ powders were mixed with 0.5–2 mol % $Al_2O_3$ additive and pressed into a pellet form of 8 mm in diameter and 10 mm in thickness. The pellet was covered with the same powder and placed in a quartz tube that was surrounded by quartz wool. Quartz was used as sample container and heat-insulating material because $SiO_2$ is transparent to microwaves.

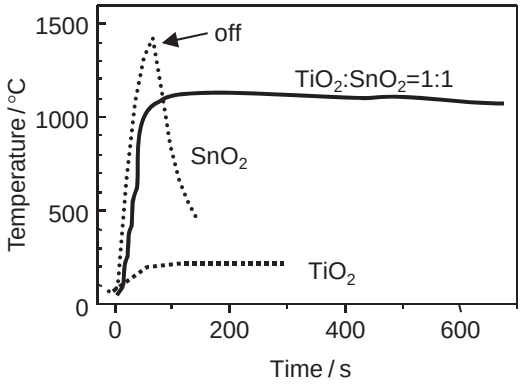


**Figure 1.** Temperature–time profiles of $SnO_2$, $TiO_2$, and $TiO_2$–$SnO_2$ mixture under irradiation of 28-GHz microwaves at 3.0-kW power output.

Microwave irradiation was carried out on the pellet specimen using a multimode microwave heating system operating at a frequency of 28 GHz (Model FMS-10-28, Fuji Dempa Kogyo Co., Ltd., Japan). The temperature of the specimen was monitored during microwave irradiation by a Pt-sheathed Pt–Pt/10% Rh thermocouple that was directly inserted into the specimen. After irradiation, the specimen was characterized by X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), and UV–vis diffuse reflectance spectroscopy.

Figure 1 shows the temperature–time profiles of $TiO_2$–$SnO_2$ mixture and the respective end members under microwave irradiation at 3.0-kW power output. $SnO_2$ strongly absorbs microwaves and can be heated rapidly above 1300 °C within a minute. In contrast, $TiO_2$ exhibited a moderate temperature increase with a saturation temperature of 200 °C. Such a difference causes a selective heating behavior, and hence the reaction between $TiO_2$–$SnO_2$ proceeds by the microwave energy absorbed by $SnO_2$, at the early stage of the reaction.

Figure 2 shows the XRD patterns of $TiO_2$–$SnO_2$ solid solution mode by microwave irradiation. It should be noted that single-phase rutile-type solid solution ($Ti_{0.5}Sn_{0.5}O_2$) could be obtained within 180 s of irradiation although the maximum temperature of the mixture was 1100 °C (see Figure 1), at which the system is in two-phase separation region (inside the miscibility dome) in equilibrium phase diagram.[7] In the diffraction pattern of the specimen irradiated for 900 s, splitting was observed for diffraction peaks with $hkl$: $l \neq 0$, suggesting [00$l$] coherent spinodal decomposition. Addition of $Al_2O_3$ enhanced the spinodal decomposition. TEM observation (Figure 3) revealed the formation of modulated lamellar structure within a grain. Energy dispersive X-ray fluorescence spectroscopy (EDX) analysis confirmed that the bright and dark regions consisted of Ti-rich

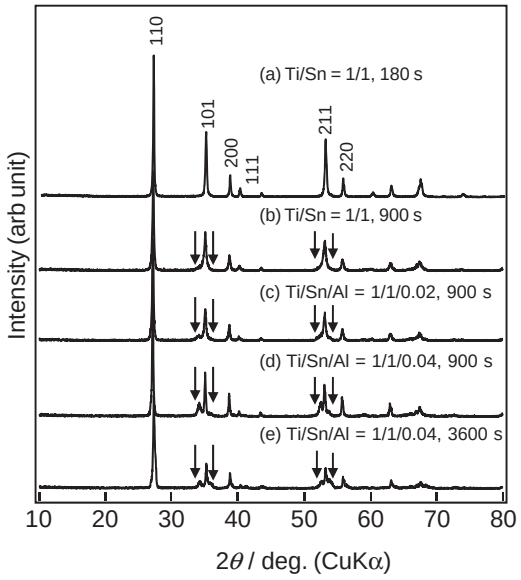


**Figure 2.** XRD patterns of $TiO_2$–$SnO_2$ solid solutions made by microwave irradiation.

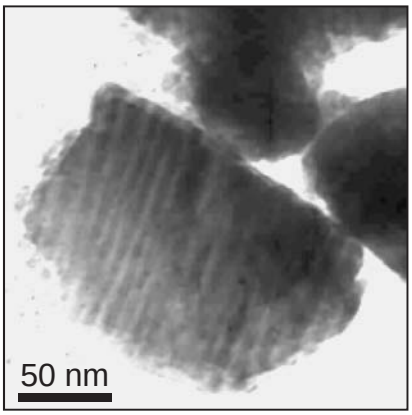


**Figure 3.** TEM photograph of $TiO_2$–$SnO_2$ grain obtained by microwave irradiation (Ti/Sn/Al = 1/1/0.02, 900 s).

($Ti_{0.72}Sn_{0.28}O_2$) and Sn-rich ($Sn_{0.71}Ti_{0.28}Al_{0.01}O_2$) solid solutions, respectively.

It was found that the modulation periodicity could be controlled by the amount of $Al_2O_3$ additive and the microwave irradiation time. Increasing the $Al_2O_3$ content and/or prolonged microwave irradiation resulted in well-developed lamellar structure.

Figure 4 shows the UV–vis diffuse reflectance spectra of $TiO_2$–$SnO_2$ (Ti/Sn = 1/1) after spinodal decomposition. The band gap energy ($E_g$) of the solid solution (ss) before spinodal decomposition is estimated to be $E_g = 3.30$ eV. The $E_g$ value decreases to 3.15 eV with increasing the modulation periodicity.

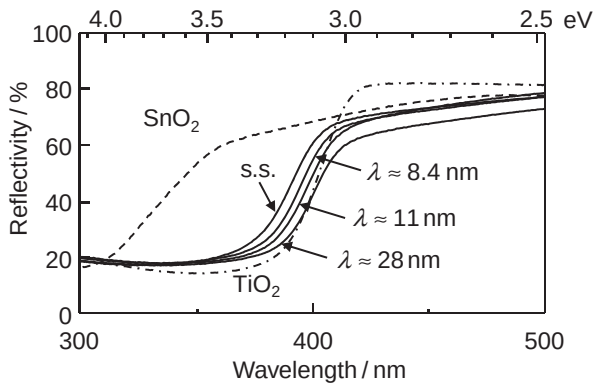


**Figure 4.** UV–vis diffuse reflectance spectra of modulated $TiO_2$–$SnO_2$ composites (Ti/Sn = 1/1) with various modulated lamellar thickness ($\lambda$).

In the binary $TiO_2$–$SnO_2$ system, lower temperature limit of the solid solution region is 1400 °C at the composition $TiO_2$:$SnO_2$ = 1:1, and the composition exhibits phase separation below 1400 °C.[7] In this study, however, formation of solid solution was completed at 1100 °C in a short period. The results suggest the following mechanism of the formation of the mesoscopic structure. When the mixture of $TiO_2$ and $SnO_2$ was irradiated with microwave, $SnO_2$ species are selectively heated to a higher temperature and react with $TiO_2$ species to form $Ti_{1-x}Sn_xO_2$ solid solution. Anisothermal condition is maintained in a certain period, and the temperature fluctuation within a microscopic scale induces spinodal decomposition, consequently, the formation of mesoscopic lamellar structure.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area, Science and Technology of Microwave-Induced, thermally Non-Equilibrium Reaction Field, from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

## References

1 D. M. P. Mingos, D. R. Baghurst, *Chem. Soc. Rev.* **1991**, *20*, 1.
2 T. Kimura, H. Takizawa, K. Uheda, T. Endo, M. Shimada, *J. Am. Ceram. Soc.* **1998**, *81*, 2961.
3 M. Iwasaki, H. Takizawa, K. Uheda, T. Endo, M. Shimada, *J. Mater. Chem.* **1998**, *8*, 2765.
4 H. Takizawa, K. Uheda, T. Endo, *J. Am. Ceram. Soc.* **2000**, *83*, 2321.
5 H. Takizawa, N. Haze, K. Okamoto, K. Uheda, T. Endo, *Mater. Res. Bull.* **2002**, *37*, 113.
6 H. Takizawa, M. Iwasaki, *IEICE Trans. Electron.* **2003**, *E86-C*, 2469.
7 M. Park, T. E. Mitchell, A. H. Heuer, *J. Am. Ceram. Soc.* **1975**, *58*, 43.
8 T. C. Yuan, A. V. Virkar, *J. Am. Ceram. Soc.* **1988**, *71*, 12.

Published on the web (Advance View) May 31, 2008; doi:10.1246/cl.2008.714