Solid-state Synthesis of Sn$_2$TiO$_4$: A New Synthetic Strategy for Direct Synthesis of Sn^{2+} Compounds Using Microwave Irradiation

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Divalent tin compound, Sn$_2$TiO$_4$, was synthesized by a simple solid-state reaction of component oxides under 2.45 GHz microwave irradiation. The reaction rapidly proceeds with the diffusion of hot Sn^{2+} species toward TiO$_2$ to form Sn$_2$TiO$_4$ within 1 min. A drastic enhancement of reaction kinetics could be achieved under thermally nonequilibrium conditions induced by strong coupling of SnO with microwave energy. This makes it possible to avoid the disproportionation reaction of SnO to Sn and SnO$_2$, giving us a new synthetic strategy for direct synthesis of Sn^{2+} compounds.

Divalent tin ion (Sn^{2+}) possesses [Kr]4d^{10}5s^2 electron configuration. The existence of stereoactive lone pair (5s^2) is an issue of concern of Sn^{2+} compounds in view of crystal chemistry and, more practically, their functionality such as occurrence of ferroelectricity. Although Sn^{2+} compounds are thought to be candidates to replace analogous Pb^{2+} compounds in various functional materials like ferroelectric PZT, only a few compounds are reported to adopt Sn^{2+} valence state in complex oxides.[1–5]

Solid-state reaction between component oxides is the most widely used method for the preparation of complex oxides; however, this cannot be applied to the synthesis of oxides containing Sn^{2+} because of the disproportionation reaction of SnO to Sn metal and SnO$_2$ above 300 °C. From this reason, other preparative methods like ion exchange using molten SnCl$_2$[4,5] and low-temperature solvothermal processing[6] have been applied for the synthesis of Sn^{2+} compounds. Recently, Kumada et al. reported a new Sn^{2+} compound, Sn$_2$TiO$_4$, synthesized by an ion-exchanging reaction between potassium titanates and SnCl$_2$.[5]

We report here a new synthetic strategy for a direct solid-state reaction to obtain Sn^{2+} compound, Sn$_2$TiO$_4$, using a thermally nonequilibrium reaction field induced by microwave selective heating. Microwave heating is a self-heating process that occurs via direct absorption of electromagnetic energy. The resultant heat can be used to drive a chemical reaction with other components.[7] Since the microwave heating behavior strongly depends on the nature of the irradiated material, a specific component in a chemical reaction system can be selectively heated to higher temperature. Such a situation causes anisothermal conditions within reaction components to form a non-equilibrium structure.[8]

Powders of TiO$_2$ (>99.9% in purity) and SnO (>99.5% in purity) were used as starting materials. These powders were mixed in the desired proportion (TiO$_2$:SnO = 1:2) and pressed into pellets 8 mm in diameter and 2 mm in thickness. The pellets were put into an alumina crucible covered with quartz glass wool. The crucible was placed in a thermal insulator made from Al$_2$O$_3$–
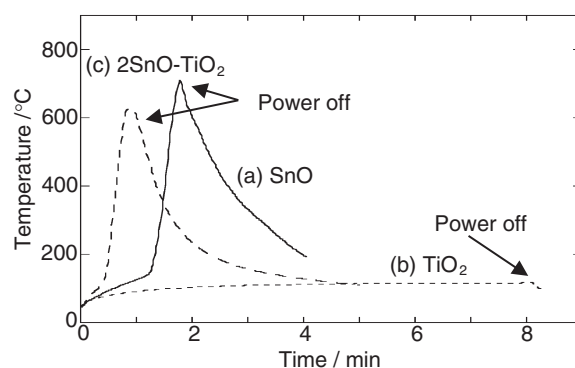

Figure 1. Temperature–time profiles of SnO, TiO$_2$, and 2SnO–TiO$_2$ mixture under microwave irradiation (2.45 GHz, 750 W).

SiO$_2$ fire brick. Microwave irradiation was carried out on the pellet specimen using a microwave heating system operating at a frequency of 2.45 GHz (Model SMW-099, Shikoku Instrumentation Co., Ltd., Japan), which allows the electromagnetic field to be focused by tuning three stub tuners or E–H tuner. The detailed setup of the microwave heating system is described in our previous paper.[9] After microwave irradiation, the specimen was characterized by X-ray diffraction (XRD) analysis and thermogravimetry–differential thermal analysis (TG-DTA). The crystal structure was refined by the Rietveld analysis of the powder X-ray diffraction data using the Rietan-2000 program.[10]

Figure 1 shows the temperature–time profiles of TiO$_2$–SnO mixture and the respective end members under microwave irradiation at 750 W power output under nitrogen atmosphere. It is obvious that SnO strongly absorbs microwaves and can be heated rapidly to 600 °C. In contrast, TiO$_2$ is nearly transparent to microwaves. Such a difference causes a selective heating behavior, and hence the reaction between TiO$_2$–SnO proceeds by the microwave energy absorbed by SnO, at the early stage of the reaction.

Figure 2 shows the XRD pattern of the TiO$_2$–SnO mixture after 1 min of microwave irradiation in nitrogen atmosphere. For comparison, the XRD data of a specimen conventionally heated to 600 °C using an electric furnace is also shown. It is obvious that the target phase, Sn^{2+}$_2$TiO$_4$, could be obtained as major phase in a short period (ca. 1 min) by microwave irradiation although slight amounts of unreacted TiO$_2$, Sn, and SnO$_2$ coexisted. The existence of Sn and SnO$_2$ is due to the disproportionation reaction of residual SnO during the cooling period. In contrast, only disproportionation was observed in conventionally heated specimens.

In order to confirm the formation of Sn$_2$TiO$_4$, the XRD data was analyzed by the Rietveld method using the single crystal
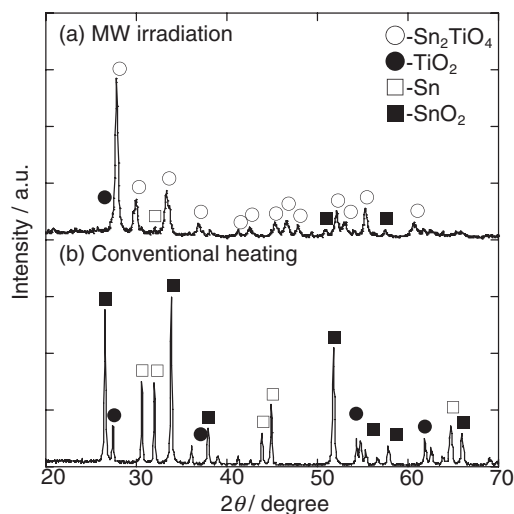
Figure 2. XRD patterns of the products obtained by (a) microwave irradiation and (b) conventional heating.
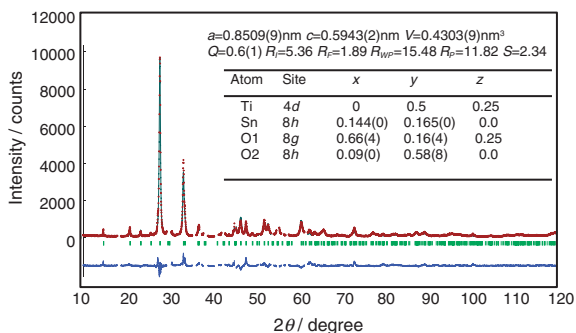

Figure 3. The results of the Rietveld analysis of the XRD data of Sn_2TiO_4.

Figure 4. TG-DTA curves for Sn_2TiO_4 measured in air. The specimen contained small amounts of Sn, SnO_2, and TiO_2 as inpurities.

structural data reported by Kumada et al.[5] The profile-fit and the difference patterns of the Rietveld analysis are shown in Figure 3. Here, some 2θ regions were exclude from the calculation due to existence of impurity phases. The final refinement gave the reliability factors of $R_I = 5.36\%$ and $R_F = 1.89\%$. The obtained lattice parameters and crystallographic parameters are in good agreement with the single-crystal data, suggesting the successful synthesis of Sn_2TiO_4.

TG-DTA measurement of the product under nitrogen atmosphere revealed that Sn_2TiO_4 is stable up to the melting point (at around 1000 °C). Figure 4 shows the TG-DTA curves measured in air, showing two-step oxidation of the product. The XRD analysis of the heat-treated specimen revealed that the first step weight gain at around 300 °C corresponds to the oxidation of metallic Sn involved as impurity phase. The second one corresponds to the oxidation of Sn_2TiO_4 above 500 °C. The weight gain of 7.1% agreed with the total oxidation of Sn^{2+} to Sn^{4+}.

In this study, a Sn^{2+} compound, Sn_2TiO_4, could be synthesized within a short period by a simple solid-state reaction under microwave irradiation. Although the reaction mechanism is still not clear, it is not doubtful that thermally nonequilibrium conditions, induced by microwave irradiation, plays a key role to form 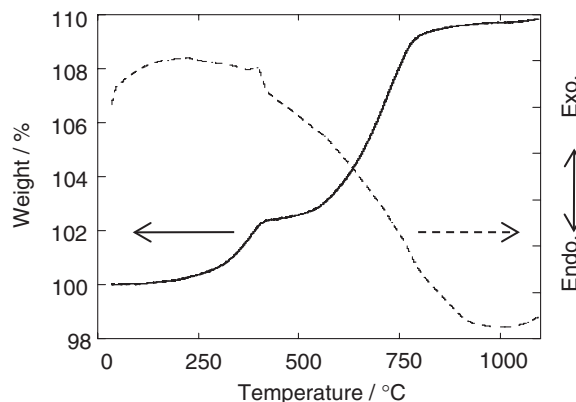a Sn^{2+} compound. Chemical reaction under microwave irradiation proceeds essentially in nonequilibrium manner because microwave heating is a self-heating process that strongly depends on the microwave–material interaction. In the present case, SnO strongly couples with microwave energy but TiO_2 does not. The reaction possibly proceeds with the diffusion of hot Sn^{2+} species toward TiO_2 to form Sn_2TiO_4. A drastic enhancement of reaction kinetics could be achieved under thermally nonequilibrium condition induced by strong coupling of SnO with microwave energy. This makes it possible to synthesize Sn^{2+} compounds, avoiding the disproportionation reaction. The present study strongly suggests that microwave processing is effective in synthesizing Sn^{2+} compounds by solid-state reaction. From this point, a survey of new Sn^{2+} compounds by microwave processing would become an attractive field in the near future.

References
1 W. Jeitschko, A. W. Sleight, *Acta Crystallogr., Sect. B* **1974**, *30*, 2088.
2 T. S. Ercit, P. Cerny, *Can. Mineral.* **1988**, *26*, 899.
3 H. Mizoguchi, A. Wattiaux, R. Kykyneshi, J. Tate, A. W. Sleight, M. A. Subramanian, *Mater. Res. Bull.* **2008**, *43*, 1943.
4 H. Mizoguchi, A. W. Sleight, M. A. Subramanian, *Mater. Res. Bull.* **2009**, *44*, 1022.
5 N. Kumada, Y. Yonesaki, T. Takei, N. Kinomura, S. Wada, *Mater. Res. Bull.* **2009**, *44*, 1298.
6 Y. Xie, S. Yin, H. Yamane, T. Hashimoto, H. Machida, T. Sato, *Chem. Mater.* **2008**, *20*, 4931.
7 D. M. P. Mingos, D. R. Baghurst, *Chem. Soc. Rev.* **1991**, *20*, 1.
8 H. Takizawa, A. Hagiya, T. Aoyagi, Y. Hayashi, *Chem. Lett.* **2008**, *37*, 714.
9 T. Aoyagi, Y. Hayashi, H. Takizawa, *Mater. Trans.* **2008**, *49*, 879.
10 F. Izumi, T. Ikeda, *Mater. Sci. Forum* **2000**, *321–324*, 198.