

Microwave Assisted Solvothermal Synthesis of a New Compound, Pyrochlore-Type $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$

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Nanopowder of a new tin(II) titanium(IV) oxide hydroxide fluoride, $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$, with the pyrochlore-type structure (cubic $a = 10.3777(7)$ Å, space group $Fd\bar{3}m$) was prepared at 180 °C and pH 2 by using a microwave assisted solvothermal reaction. The grain size of the nanopowder was 20–30 nm. It decomposed into a mixture of anatase-type and rutile-type $\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_2$ at around 400 °C. A single phase of rutile-type $\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_2$ (tetragonal $a = 4.6805(6)$, $c = 3.0961(4)$ Å, space group $P4_2/mnm$) having a grain size of about 100 nm could be obtained by heating $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$ at 800 °C.

1. Introduction

Inorganic lead compounds are widely used as stabilizers of polyvinylchloride, heat-resistant stabilizers of rubber, piezoelectric ceramics, visible light responsive photocatalysts, and so forth,^{1,2} and contained in many products such as colors and paints. However, the use of lead causes environmental problems due to its toxicity. It is now necessary and imperative to develop environmentally friendly lead-free materials to replace the lead-based ceramics.³ The properties of Pb(II) materials arise due to the presence of lone-pair electrons in Pb^{2+} . Sn which is located just above Pb on the periodic table of elements belongs to the group IV elements just like Pb. Thus, the electrical configurations of Sn(II) compounds may be similar to those of Pb(II) compounds. It was actually reported that Sn(II) niobate and tantalate showed visible light responsive photocatalytic activity similar to Pb(II) niobate and tantalate.^{2,4} It is also estimated that Sn(II) titanate shows excellent ferroelectricity similar to Pb(II) titanate by first principles calculations.^{5–10} However, Sn(II) titanate cannot be obtained via conventional ceramic processing routes, that is, solid state reaction, because of the disproportionation reaction of Sn(II) to Sn and Sn(IV) at high temperatures. A solvothermal process in which water and/

or nonaqueous solvent is used as a reaction medium is a powerful method for the synthesis of well dispersed ceramic nanoparticles under mild conditions since the chemical reaction of inorganic materials can be greatly accelerated under solvothermal conditions.^{11–14} Thus, a solvothermal process seems to be one of the best ways to realize the low temperature synthesis of Sn(II) titanate. We have first succeeded in synthesizing a new pyrochlore-type compound $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$ as a single phase by microwave assisted solvothermal reaction.¹⁵ In the present study, the optimization for the synthesis of $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$ nanoparticles by the microwave assisted solvothermal reaction and characterization of the product was conducted.

2. Experimental Section

2.1. Microwave Assisted Solvothermal Synthesis. Reagent grade SnF_2 and $\text{Ti}(i\text{-C}_3\text{H}_7\text{O})_4$ were used as starting materials. Initially, a 10 cm³ portion of 0.5 M SnF_2 aqueous solution and a 10 cm³ portion of 0.5 M $\text{Ti}(i\text{-C}_3\text{H}_7\text{O})_4$ *i*-propanol solution were mixed under stirring, and then a desired amount of ammonia aqueous solution was added into the mixture to change the pH of the starting solution. Then, the solution was diluted to 40 cm³ and transferred to a Teflon reaction vessel of 70 cm³ internal volume and was irradiated by microwave to start the solvothermal reaction in the temperature range of 160–230 °C for 10–60 min using a microwave reaction apparatus (ACTAC Co., MWS-2). After reaction, the precipitate was collected with a centrifuge and rinsed with ethanol, deionized water, and acetone three times, respectively. Then the obtained powders were dried overnight at 60 °C in a vacuum oven.

2.2. Characterization. The X-ray diffraction (XRD) of the obtained powder samples was carried out using $\text{Cu K}\alpha$ radiation with a pyrolytic graphite monochromator mounted on a powder

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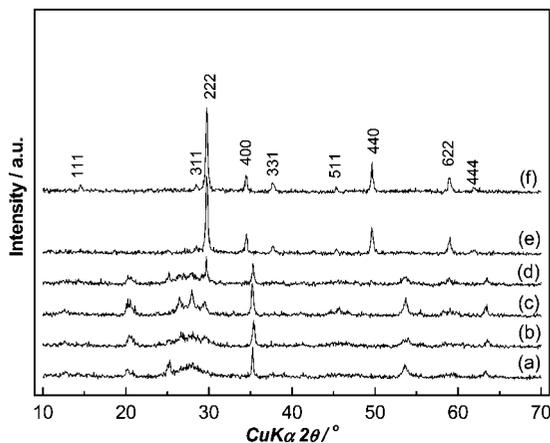


Figure 1. XRD patterns of samples obtained at 180 °C and at pH > 13 (a), pH = 7 (b), pH = 6 (c), pH = 5 (d), pH = 4 (e), and pH = 2 (f) for 30 min. The peaks from the cubic pyrochlore-type compound are indexed in (f).

diffractometer (Shimadzu XD-D1). Sn and Ti contents were analyzed using a powder of 20 mg from a sample by inductively coupled plasma–optical emission spectrometry–emission spectroscopy (ICP, Thermo Fisher Scientific, IRIS Advantage Duo). The oxygen contents were determined with a sample of about 1 mg by the helium carrier fusion-infrared absorption (LECO, TC-436). Hydrogen content was measured with a 2 mg sample by the C, H, N analysis (Yanaco, CHN CORDER MT-6). Measurement was carried out three times for the analysis of Sn, Ti, and O and two times for hydrogen. The average values were taken as the results. The estimated uncertainties were approximately ± 0.5 mass %. Qualitative X-ray fluorescence (WDX) analysis (RIGAKU, ZSX Primus II) was adopted to detect fluorine in the sample and the RIETAN2000 program¹⁶ was used in the Rietveld analysis of the X-ray powder diffraction pattern.

The thermogravimetric and differential thermal analyses (TG-DTA, Rigaku, TG8101D) were performed for the samples from room temperature to 1200 °C with a heating rate of 10 °C/min in air. The particle morphology was observed by using a transmission electron microscopy (JEOL, JEM-2000EX).

3. Results and Discussion

3.1. Synthesis. The process parameters of the microwave solvothermal reaction to synthesize the powder of the pyrochlore-type compound are pH, reaction temperature, and microwave heating time. Figure 1 shows the X-ray diffraction patterns of the samples synthesized by a microwave solvothermal process at 180 °C at various pHs for 30 min. It was observed that the XRD profiles changed depending on the solution pH, that is, the samples at pH 2 and 4 showed sharp XRD peaks which could be indexed with a cubic cell of the pyrochlore-type structure ($a = 10.4$ Å, space group $Fd\bar{3}m$). However, the diffraction peaks became broad, and other diffraction peaks appeared above pH 5. The single pyrochlore phase could not be obtained above pH 5. This might be related to the existence of excess OH^- and the instability of pyrochlore at high pH conditions. The XRD peaks of the powders synthesized above pH 5 were not identified. As a result, the acidic condition at pH 2 without adding ammonia was chosen for further experiments to produce the single phase of the pyrochlore-type compound.

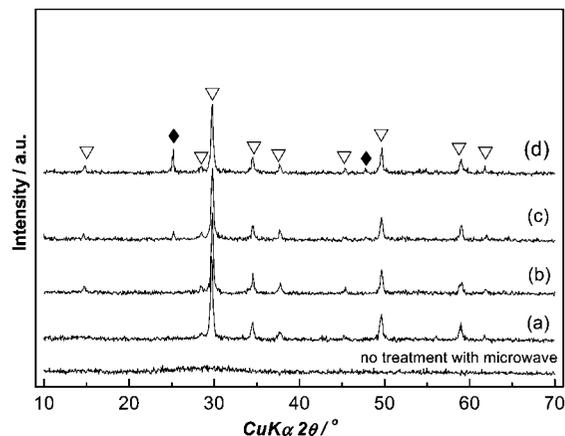


Figure 2. XRD patterns of samples synthesized at 160 °C (a), 180 °C (b), 200 °C (c), and 230 °C (d) for 1 h. ∇ , pyrochlore-type compound; \blacklozenge , anatase.

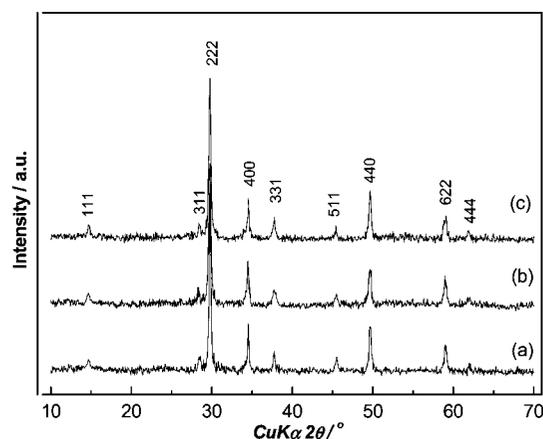


Figure 3. XRD patterns of samples treated at 180 °C and pH 2 for 10 min (a), 20 min (b), and 60 min (c).

Figure 2 shows the X-ray diffraction patterns for the samples prepared at pH 2 and at temperatures of 160, 180, 200, and 230 °C for 1 h. The sample before microwave irradiation was amorphous, but the samples obtained at 160 and 180 °C were identified as the single phase of the pyrochlore-type compound. The diffraction peaks of the sample prepared at 180 °C were sharper than those at 160 °C, while the XRD peaks attributed to anatase TiO_2 appeared in the samples obtained above 200 °C. Therefore, 180 °C was selected as the optimum temperature to synthesize the pyrochlore-type compound.

Under the selected conditions (pH = 2, 180 °C), samples were synthesized with different microwave solvothermal reaction times, and the XRD patterns of the products are presented in Figure 3. There was no remarkable difference in XRD profiles of the samples obtained for 10 min, 20 min, and 1 h, therefore confirming that the pyrochlore phase was formed quickly within 10 min under the present reaction conditions.

3.2. Chemical Composition and Crystal Structure. Chemical analyses were carried out for the pyrochlore-type compound obtained at pH = 2 and 180 °C for 10 min. The total amounts of Sn, Ti, O, and H determined by the quantitative analysis were 92 mass %. Negligible amounts of carbon and nitrogen were detected by the elemental analysis and the helium carrier fusion-infrared absorption method. A

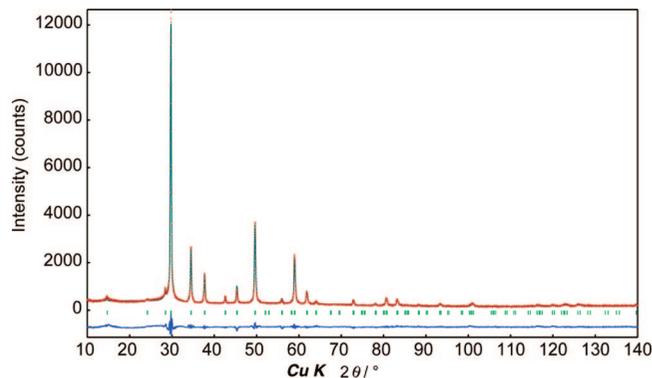


Figure 4. Observed (dots) and calculated (solid) X-ray diffraction profiles for $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$. Tick marks below the diffraction pattern represent the allowed Bragg reflections. The difference profile is located at the bottom of the figure.

Table 1. Crystallographic Data and Structure Refinement for $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$

formula	$\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$
formula weight	350.99
space group	$Fd\bar{3}m$ (Vol. A, 227, Setting #2)
unit cell dimension	10.3777(7) Å
cell volume	1117.64(13) Å ³
Z	8
density (calculated)	4.17 g/cm ³
step width/data point	0.02°/6502
number of observed peaks	47
number of refined parameters	29 (background 12, scale 1, peak form 8, lattice parameter 1, structure 7)
goodness-of-fit S	1.299
R indexes	$R_{\text{wp}} = 7.06\%$, $R_{\text{p}} = 5.48\%$, $R_{\text{I}} = 2.03\%$, $R_{\text{F}} = 2.45\%$

small characteristic X-ray peak of fluorine was detected by the XRF spectrum. Thus, we regarded the residual amount was fluorine and expressed the composition of the sample as Sn, 42.1; Ti, 26.2; O, 23.2; H, 0.5; and F, 8.0 in mass %. The molar ratio Sn:Ti:F in the product was 0.65:1:0.78. The Sn and F contents were less than those in the starting solution (Sn:Ti:F = 1:1:1), suggesting that Sn and F are more soluble than Ti at the synthetic condition.

Figure 4 shows the profile fit and difference patterns of the Rietveld analysis for the powder XRD pattern of the pyrochlore-type compound. All peaks in the observed pattern were indexed with a cubic cell $a = 10.3777(7)$ Å (space group $Fd\bar{3}m$). The pattern is similar to the XRD patterns of pyrochlore compounds such as $\text{Eu}_2\text{Ti}_2\text{O}_7$ ($a = 10.2064(5)$ Å),¹⁷ $\text{Ca}_2\text{Ta}_2\text{O}_6\text{F}$ ($a = 10.421(2)$ Å),¹⁸ and $(\text{K}_{1.14}\text{Bi}_{0.37})\text{Bi}_2(\text{O}_{4.9}(\text{OH})_{1.1})(\text{OH})_{0.8}$ ($a = 10.965(1)$ Å).¹⁹ The crystallographic data of the pyrochlore-type compound are summarized in Table 1. Site occupancies, atomic coordinates, and displacement parameters are listed in Table 2. Conventional agreement factors $R_{\text{wp}} = 7.06\%$, $R_{\text{p}} = 5.48\%$, $R_{\text{I}} = 2.03\%$, and $R_{\text{F}} = 2.45\%$ were obtained by the refinement. Figure 5 shows the crystal structure drawn with VESTA.²⁰ In the structure refinement with a model of the pyrochlore-

Table 2. Structure Parameters of $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$

atom	site	g	x	y	z	$B, \text{Å}^2$
Sn	16d	0.620(3)	1/2	1/2	1/2	7.22(7)
Ti1	16c	0.891(4)	0	0	0	2.58(7)
Ti2	8a	0.157(4)	1/8	1/8	1/8	2.58 ^b
O/F1 ^a	48f	1.0	0.3034(3)	1/8	1/8	2.58 ^b
O/F2 ^a	8b	0.58(15)	3/8	3/8	3/8	7.22 ^c

^a Fraction of O and F: 0.784:0.216 ^b Constrained with the value of $B(\text{Ti1})$. ^c Constrained with the value of $B(\text{Sn})$.

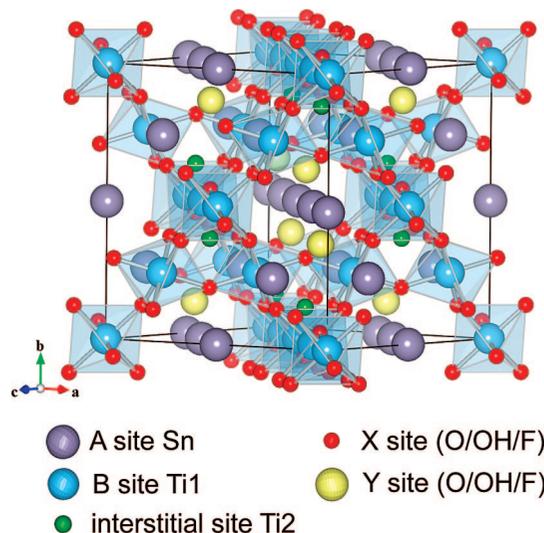


Figure 5. Crystal structure of $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$.

type structure denoted with $\text{A}_2\text{B}_2\text{X}_6\text{Y}$, the anion sites of X (Wyckoff 48f site) and Y (8b site) were occupied with O and F statistically in accordance with a ratio O:OH:F = 0.556:0.228:0.216 (O:F = 0.784: 0.216) determined by the chemical analysis because their electron scattering powers were very close. The refined parameter x of the 48f site was 0.3034(3), which was in accordance with that of other reported pyrochlore-type compounds, for example, $\text{Eu}_2\text{Ti}_2\text{O}_7$, $x = 0.328(1)$,¹⁷ and $\text{Ca}_2\text{Ta}_2\text{O}_6\text{F}$, $x = 0.3173(15)$.¹⁸

The chemical formula of the structure obtained by the refinement was $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$ (Sn, 41.9; Ti, 26.4; O, 23.5; H, 0.4; and F, 7.7 in mass %), which agreed with the composition determined by the chemical analysis in the range of the experimental errors. The structural formula of the compound is expressed as $[\text{Sn}^{2+}_{0.62}\square_{0.38}]_{2.00}[\text{Ti}^{4+}_{0.89}\square_{0.11}]_{2.00}(\text{Ti}^{4+}_{0.16}\square_{0.84})[\text{O}^{2-}_{0.556}(\text{OH})^{-}_{0.228}\text{F}^{-}_{0.216}]_{6.00}[\text{O}^{2-}_{0.322}(\text{OH})^{-}_{0.132}\text{F}^{-}_{0.125}\square_{0.420}]$. The B site (Ti1, 16c) is occupied by Ti^{4+} atoms with an occupation factor of 0.89. A small number of Ti^{4+} also occupies an interstitial 8a site (Ti2, 8a). The interstitial site is between the B sites and octahedrally surrounded by the six X sites with a distance of 1.852(3) Å which is a little shorter than the Ti1–X distance (1.9165(9) Å).

As illustrated in Figure 5, Ti1-centered X anion octahedra form three-dimensional cages by sharing apical X-anion. The A (16d) and Y (8b) sites were in the tunnels of the cages. 62% of the A site, which is at 2.744(2) Å from the X site, is occupied by Sn^{2+} . Y site is surrounded by four A sites with a distance of 2.2468(1) Å. An A-site defect pyrochlore-type structure was reported for $\text{TiTiNbO}_4\text{F}_2$ ($a = 10.365(3)$ Å, the structure formula $(\text{Ti}^{4+}_{0.5}\square_{0.5})_{2.00}(\text{Ti}^{4+}_{0.5}\text{Nb}^{5+}_{0.5})_{2.00}$

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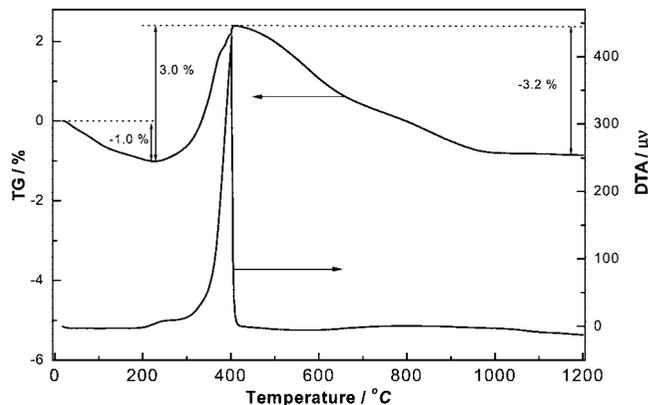


Figure 6. TG-DTA curves of $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$ prepared at pH 2 and 180 °C for 10 min.

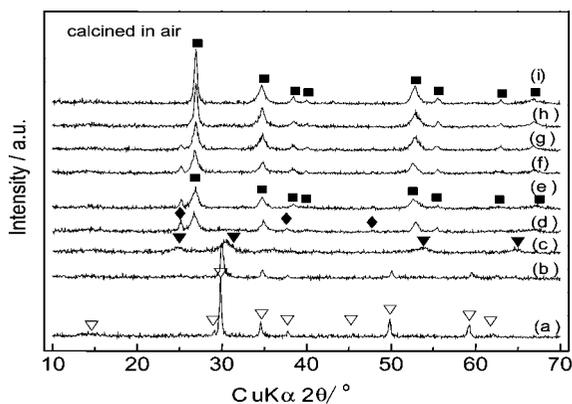


Figure 7. XRD patterns of $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$ calcined at 200 °C (a), 300 °C (b), 350 °C (c), 400 °C (d), 500 °C (e), 600 °C (f), 700 °C (g), 800 °C (h), and 900 °C (i) for 1 h. ▽, pyrochlore-type compound; ▼, brookite-type; ◆, anatase-type; □, rutile-type $\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_2$.

($\text{O}^{2-}_{0.667}\text{F}^{-}_{0.333}$) $_{6.00}$ □ $_{1.00}$) $_{21}$ where the Y site is vacant. This structure was refined with a common atomic displacement parameter of 13.6 Å² for all sites. During our structure refinement, the isotropic displacement parameters B of Sn and F2 atoms were constrained with a same parameter. The refined value was 7.22(7) Å², which was fairly larger than the normal values expected for inorganic substances but smaller than the value reported for $\text{TiTiNbO}_4\text{F}_2$.²¹ The large value suggests deviation of the actual atomic positions from the ideal positions of 16c and 8b sites in the local structure as well as the large thermal motion in the cages.

3.3. Thermal Stability and Micro(Nano) Structures.

The TG-DTA curves of $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$ prepared at pH 2 and 180 °C for 10 min are shown in Figure 6. The sample showed small weight loss of approximately 1% from room temperature to up to 200 °C, probably due to the release of water adsorbed on the surface and then followed by a large weight gain above 300 °C with a sharp exothermic peak at 375 °C. This large weight gain may be due to the oxidation of Sn^{2+} to Sn^{4+} leading to a phase change (or decomposition), and the weight loss above 400 °C may be due to the elimination of OH as water molecules and/or F.

To confirm the phase change behavior, the XRD of the samples calcined at different temperatures for 1 h was

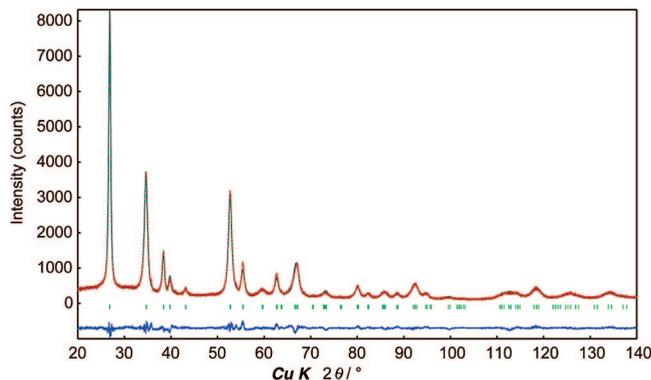


Figure 8. Observed (dots) and calculated (solid) X-ray diffraction profiles for $\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_2$. Tick marks below the diffraction pattern represent the allowed Bragg reflections. The difference profile is located at the bottom of the figure.

Table 3. Crystallographic Data and Structure Refinement for $\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_{2.00}$

formula	$\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_{2.00}$
formula weight	107.46
space group	$P4_2/mmm$ (Vol. A, 136)
unit cell dimension	$a = 4.6805(6)$, $c = 3.0961(4)$ Å
cell volume	67.826(16) Å ³
Z	2
density (calculated)	5.26 g/cm ³
step width/data point	0.02°/5601
number of observed peaks	42
number of refined parameters	29 (zero shift 1, background 12, scale 1, peak form 8, lattice parameter 1, structure 6)
goodness-of-fit S	1.419
R indexes	$R_{\text{wp}} = 7.15\%$, $R_{\text{p}} = 5.36\%$, $R_{\text{I}} = 1.56\%$, $R_{\text{f}} = 0.84\%$

Table 4. Structure Parameters of $\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_{2.00}$

atom	site	g	x	y	z	B/Å ²
Sn/Ti	2a	0.390/0.610(11)	0	0	0	0.28(3)
O	4f	1	0.3059(5)	0.3060	0	1.99(15)

performed as shown in Figure 7. It could be observed that the sample calcined at 300 °C still retained the pyrochlore-type structure although the peak intensity became weaker. The broad peaks at 24.8°, 30.5°, and 53.8° in 2θ appeared in the XRD pattern of the sample heated at 350 °C were probably related to the brookite-type structure. At 400 °C, the pyrochlore-type phase completely changed into a mixture of anatase-type and rutile-type compounds. With increasing temperature, the anatase phase gradually disappeared and at 800 °C a single phase of rutile-type compound was obtained.

Rutile-type SnO_2 - TiO_2 phases were prepared at around 1450 °C by a conventional solid state reaction.²² $\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_2$ obtained in the present study is a metastable phase because usually the TiO_2 - SnO_2 solid solution separates into Sn-rich and Ti-rich rutile type solid solution phases at 800 °C (spinodal decomposition) according to the SnO_2 - TiO_2 phase diagram by Schultz and Stubican²³ and by Park et al.²⁴ The lattice parameters of $\text{Sn}_x\text{Ti}_{1-x}\text{O}_2$ have been determined

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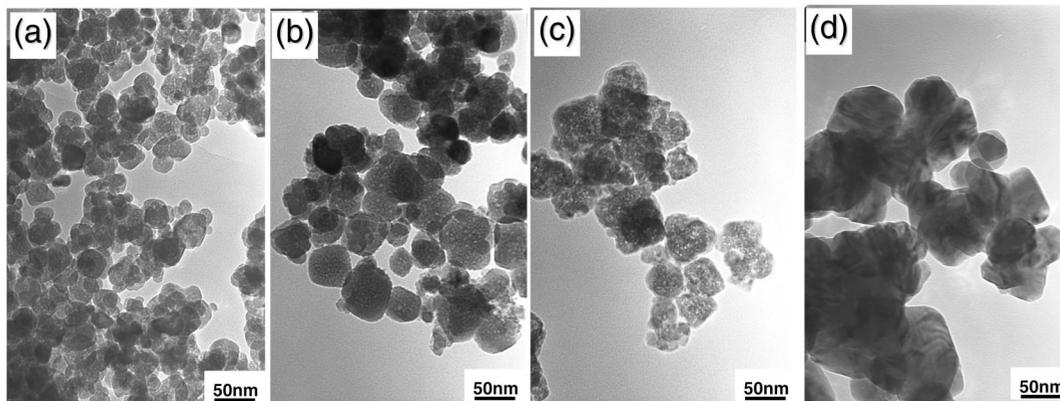


Figure 9. TEM images of $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$ (a) and powder obtained by heating of $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$ at 200 °C (b), 350 °C (c), and 900 °C (d).

experimentally.^{22–25} Hirata estimated theoretically the positional parameter u of O atoms that occupy the $4f$ sites $6(u,u,0)$ of the space group $P4_2/mnm$ of the rutile-type structure, because no data for the solid solutions existed although the data are available for the end members of TiO_2 and SnO_2 .²⁶ Figure 8 shows the XRD pattern of $\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_2$ prepared by heating at 800 °C for 1 h and the pattern by the Rietveld analysis. Table 3 lists the crystallographic data and structure refinement for $\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_2$, and Table 4 shows the occupancies, atomic coordinates, and displacement parameters. The Sn:Ti ratio of 0.390:0.610(11), determined by the Rietveld refinement with good agreement factors shown in Table 3, agreed with that of $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$. The refined lattice parameters of $a = 4.6805(6)$ and $c = 3.0961(4)$ Å and the oxygen positional parameter $u = 0.3059(5)$ were identical with those reported by Hirata ($a = 4.6804$, $c = 3.0955$ Å, and $u = 0.66138$ for $x = 0.4$).²⁶ Therefore, it was concluded that the pyrochlore-type phase undergoes phase decomposition into the brookite-type phase at around 350 °C, and the mixture of anatase- and rutile-type phases at 400–700 °C, and then the single phase of rutile-type $\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_2$ at around 800 °C, which corresponded to the changes observed in the TG-DTA data shown in Figure 6.

Figure 9 shows the TEM images for $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$ prepared by the microwave assisted solvothermal reaction at pH 2 and 180 °C for 10 min and those calcined at different temperatures. The as-prepared sample

consisted of nanoparticles with an average particle diameter of about 20–30 nm. The particle size slightly increased after calcination at 200 °C. The sample calcined at 350 °C consisted of agglomerated particles of ca. 50 nm in diameter, which consisted of much smaller nanoparticles and some holes. The particle size of $\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_2$ formed by calcination at 900 °C became larger, yet the particle size was still around 100 nm. The particle size of $\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_2$ formed in the present reaction is much smaller than that produced by the conventional solid state reaction at around 1450 °C.²²

4. Conclusions

On the basis of the foregoing evidence, a new compound $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$ showing the formal valence of Sn(II) was obtained as nanoparticles of 20–30 nm in diameter by a microwave assisted solvothermal reaction. It crystallizes in a cubic cell with the pyrochlore-type structure. The pyrochlore-type compound decomposed into rutile-type $\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_2$ around 800 °C. The particles of $\text{Sn}_{0.39}\text{Ti}_{0.61}\text{O}_2$ formed using the synthesized compounds as a precursor also consisted of nanoparticles of approximately 100 nm in diameter.

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