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Sol–gel synthesis of nanosized $\lambda$-Ti$_3$O$_5$ crystals

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Abstract. In this study, we show a synthesis of $\lambda$-Ti$_3$O$_5$ nanocrystals dispersed in silica by sol–gel method. The X-ray diffraction measurements, Rietveld analyses, and transmission electron microscope images of the obtained samples showed that tuning the sintering temperature in the synthesis process can control the size of the $\lambda$-Ti$_3$O$_5$ nanocrystals, i.e., 8±2 nm (1123°C; sample 1), 9±3 nm (1133°C; 2), 9±2 nm (1143°C; 3), 10±3 nm (1153°C; 4), 11±4 nm (1163°C; 5), 13±4 nm (1173°C; 6), 25±12 nm (1200°C; 7), and 36±15 nm (1250°C; 8), whereas adjusting the hydrogen flow rate can tune the oxidation-reduction state of the sample without apparent change in the crystal size. At the lowest sintering temperature of 1123°C, the smallest $\lambda$-Ti$_3$O$_5$ nanocrystals of 8 nm in size were produced.

1. Introduction

Photo-induced phase transition materials such as chalcogenides are attractive for both fundamental and applied research [1–4]. Chalcogenides are used as the recording phase-change material in storage media, e.g., Digital versatile discs (DVDs) and Blu-ray discs. However, because chalcogenides are comprised of rare and expensive elements, numerous researchers are exploring new materials that can replace chalcogenides in next-generation optical storage media [5–19].

In our efforts to find a suitable next-generation optical storage medium, we synthesized Ti$_3$O$_5$ nanoparticles with a novel phase, $\lambda$-Ti$_3$O$_5$, in 2010 [20]. Irradiating $\lambda$-Ti$_3$O$_5$ with laser light at room temperature causes a reversible photo-induced metal-to-semiconductor phase transition between black metallic $\lambda$-Ti$_3$O$_5$ and brown semiconducting $\beta$-Ti$_3$O$_5$ (figure 1). $\lambda$-Ti$_3$O$_5$ is an environmentally friendly and sustainable material that consists of highly abundant elements [21,22]. Consequently, $\lambda$-Ti$_3$O$_5$ is a promising candidate for use in rewritable recording optical media.

The morphology of $\lambda$-Ti$_3$O$_5$ depends on its synthesis [20]. A combination of reverse–micelle and sol–gel techniques provides $\lambda$-Ti$_3$O$_5$ nanocrystals dispersed in a SiO$_2$ matrix, where the nanocrystal size is 21±11 nm. In contrast, a sintering method, such as sintering titanium dioxide (TiO$_2$) nanoparticles, provides the flake form $\lambda$-Ti$_3$O$_5$, where the $\lambda$-Ti$_3$O$_5$ size is several micrometers assembled from 25±15 nm nanocrystals. The possibility to reducing the size of $\lambda$-Ti$_3$O$_5$ is important from the viewpoints of basic and applied science. In this work, we demonstrate that tuning the sintering temperature can control...
2. Experimental
2.1. Synthesis
The sol–gel method is employed to synthesize $\lambda$-Ti$_3$O$_5$ nanocrystals (figure 2). While stirring, 9.6 ml of aqueous ammonia ($6.8 \times 10^{-2}$ mol dm$^{-3}$) was added to 420 ml of a TiCl$_4$ aqueous solution ($2.8 \times 10^{-2}$ mol dm$^{-3}$). Next, 24 ml of tetraethoxysilane (TEOS) was added, and the solution was stirred for 20 hours. Then the obtained gel was collected by centrifugation, washed with methanol and chloroform, and dried at 60°C for one day. The resulting dry powder was sintered in hydrogen at a flow rate of 0.7 L min$^{-1}$ for five hours at various temperatures, i.e., 1123°C (sample 1), 1133°C (sample 2), 1143°C (sample 3), 1153°C (sample 4), 1163°C (sample 5), 1173°C (sample 6), 1200°C (sample 7), and 1250°C (sample 8). Additional samples were prepared at a fixed sintering temperature of 1163°C for five hours, but with various hydrogen flow rates, i.e., 0.05 L min$^{-1}$ (sample 9), 0.3 L min$^{-1}$ (sample 10), 1.5 L min$^{-1}$ (sample 11), and 3.0 L min$^{-1}$ (sample 12).

2.2. Characterization
Transmission electron microscope (TEM) measurements were acquired with JEOL JEM-2000EXII. The X-ray diffraction (XRD) measurements were performed using Rigaku Ultima IV with Cu Kα radiation ($\lambda$ =1.5418 Å). Rietveld analyses were performed using the Rigaku PDXL program.

Figure 1. Schematic illustration of the reversible photo-induced metal-to-semiconductor phase transition between $\lambda$-Ti$_3$O$_5$ and $\beta$-Ti$_3$O$_5$. Light blue (gray in black and white print), purple (light gray), and dark blue (dark gray) balls represent Ti(1), Ti(2), and Ti(3) atoms of $\lambda$-Ti$_3$O$_5$, while red (gray), light red (light gray), and dark red (dark gray) balls represent Ti(1), Ti(2), and Ti(3) atoms of $\beta$-Ti$_3$O$_5$, respectively. Small gray balls represent O atoms.

Figure 2. Sol–gel synthesis of $\lambda$-Ti$_3$O$_5$. (i) Aqueous ammonia is added to an aqueous solution containing titanium chloride, yielding the sol of titanium hydroxide, Ti(OH)$_4$. (ii) TEOS, Si(OC$_2$H$_5$)$_4$, is added to the reaction solution to yield a metal hydroxide coated with a sol of silica via hydrolysis, Ti(OH)$_4$/SiO$_2$. (iii) Centrifuging and sintering the obtained gel under a hydrogen atmosphere yields $\lambda$-Ti$_3$O$_5$ nanocrystals in a SiO$_2$ matrix.
3. Results and discussion

3.1. Effect of sintering temperature

Figures 3 show the XRD patterns for samples 1–8 at room temperature. The insets show the TEM

![Figure 3](image_url)

Figure 3. Powder X-ray diffraction patterns and Rietveld analyses for samples sintered at (a) 1123°C (sample 1), (b) 1133°C (2), (c) 1143°C (3), (d) 1153°C (4), (e) 1163°C (5), (f) 1173°C (6), (g) 1200°C (7), and (h) 1250°C (8). Broad baseline caused by amorphous SiO₂ is eliminated. Red (gray in black and white print) dots and black lines are the observed plots and calculated patterns, respectively. Black and gray bars represent the calculated positions of the Bragg reflections of Ti₃O₅ and Ti₂O₃, respectively. Huge peaks of SiO₂ cristobalite are excluded from the Rietveld analyses for samples 6–8 (blank ranges). Insets show the TEM images and crystal size distribution.
images and crystal size distribution. Rietveld analyses indicate that the crystal structures of the main phases of samples 1–8 are monoclinic (space group C2/m). The obtained lattice constants as shown in table 1 are consistent with the previously reported crystal structure parameters for \( \lambda \)-Ti_3O_5 [20]. For samples 1–3, the XRD patterns indicate that the \( \lambda \)-Ti_3O_5 fraction is 100%, whereas those for samples 4–8 contain minor peaks, which are assigned to a few percent of Ti_2O_3 impurity.

Figure 4 plots the crystal size versus sintering temperature. Crystals of samples 1–8 have average sizes between 8 and 36 nm, i.e., 8±2 nm, 9±3 nm, 9±2 nm, 10±3 nm, 11±4 nm, 13±4 nm, 25±12 nm, and 36±15 nm for samples 1, 2, 3, 4, 5, 6, 7, and 8, respectively. A low sintering temperature suppresses crystal growth and the lowest sintering temperature in this study, 1123°C, produced the smallest \( \lambda \)-Ti_3O_5 nanocrystals of 8 nm in size.

### Table 1. Crystallographic data of samples 1–8, including lattice parameters of \( \lambda \)-Ti_3O_5 obtained by Rietveld refinement of the powder XRD patterns.

| Sample | 1   | 2   | 3   | 4   |
|--------|-----|-----|-----|-----|
| Sintering temperature (°C) | 1123| 1133| 1143| 1153|
| H_2 flow rate (L min\(^{-1}\)) | 0.7 | 0.7 | 0.7 | 0.7 |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | C2/m | C2/m | C2/m | C2/m |
| \( a \) (Å) | 9.832(4) | 9.799(3) | 9.832(3) | 9.806(3) |
| \( b \) (Å) | 3.7962(8) | 3.7869(5) | 3.7954(6) | 3.7931(5) |
| \( c \) (Å) | 9.962(4) | 9.973(3) | 9.984(3) | 9.997(2) |
| \( \beta \) (°) | 91.06(3) | 91.09(2) | 91.02(2) | 91.04(2) |
| \( V \) (Å\(^3\)) | 371.8(2) | 370.01(17) | 372.51(16) | 371.78(14) |
| \( Z \) | 4 | 4 | 4 | 4 |
| \( R_w p \) (%) | 1.90 | 1.92 | 1.88 | 1.85 |
| \( S \) | 1.0432 | 1.0589 | 1.0458 | 1.0363 |
| \( \lambda \)-Ti_3O_5 (%) | 100 | 100 | 100 | 95.6(4) |
| Impurity (Ti_2O_3) (%) | 0 | 0 | 0 | 4.4(4) |

| Sample | 5   | 6   | 7   | 8   |
|--------|-----|-----|-----|-----|
| Sintering temperature (°C) | 1163| 1173| 1200| 1250|
| H_2 flow rate (L min\(^{-1}\)) | 0.7 | 0.7 | 0.7 | 0.7 |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | C2/m | C2/m | C2/m | C2/m |
| \( a \) (Å) | 9.8327(18) | 9.8158(16) | 9.8244(12) | 9.8202(10) |
| \( b \) (Å) | 3.7952(3) | 3.7898(3) | 3.7829(2) | 3.7818(3) |
| \( c \) (Å) | 9.9794(15) | 9.9725(13) | 9.9545(11) | 9.9567(8) |
| \( \beta \) (°) | 91.008(11) | 91.038(9) | 91.041(8) | 91.081(5) |
| \( V \) (Å\(^3\)) | 372.34(9) | 370.92(8) | 369.90(6) | 369.71(4) |
| \( Z \) | 4 | 4 | 4 | 4 |
| \( R_w p \) (%) | 2.09 | 2.58 | 3.69 | 3.58 |
| \( S \) | 1.1845 | 1.327 | 1.8241 | 1.7675 |
| \( \lambda \)-Ti_3O_5 (%) | 95.2(4) | 91.4(4) | 94.4(5) | 97.0(6) |
| Impurity (Ti_2O_3) (%) | 4.8(4) | 8.6(3) | 5.6(3) | 3.0(3) |
3.2. **Effect of hydrogen flow rate**

Samples 9–12 were sintered at a fixed temperature of 1163°C, but the hydrogen flow rate was changed between 0.05–3.0 L min\(^{-1}\). Figures 5 show the XRD patterns of samples 9–12. The insets are

![Figure 4](image-url)

**Figure 4.** Crystal size versus sintering temperature under a hydrogen flow rate of 0.7 L min\(^{-1}\).

![Figure 5](image-url)

**Figure 5.** Powder X-ray diffraction patterns and Rietveld analyses for samples sintered at a fixed temperature of 1163°C under hydrogen flow rate of (a) 0.05 L min\(^{-1}\) (sample 9), (b) 0.3 L min\(^{-1}\) (10), (c) 1.5 L min\(^{-1}\) (11), and (d) 3.0 L min\(^{-1}\) (12). Broad baseline caused by amorphous SiO\(_2\) is eliminated. Blue (gray in black and white print) dots and black lines are the observed plots and calculated patterns, respectively. Black and gray bars represent the calculated positions of the Bragg reflections of \(\lambda\)-Ti\(_3\)O\(_5\) and TiO\(_2\) or Ti\(_2\)O\(_3\), respectively. Huge peaks of SiO\(_2\) cristobalite are excluded from the Rietveld analyses for samples 11 and 12 (blank ranges). Insets show the TEM images and crystal size distribution.
TEM images and size distribution. Rietveld analyses indicate that the main phase of sample 9 is anatase TiO$_2$, while samples 10–12 are mainly comprised of $\lambda$-Ti$_3$O$_5$ (table 2). Samples 11 and 12 contain a minor impurity phase of Ti$_2$O$_3$, and the Ti$_2$O$_3$ fraction increases as the hydrogen flow rate increases. Samples 9–12 have an average size of ten or more nanometers, i.e., varying the hydrogen flow rate has less effect on the nanocrystal size, compared to varying the sintering temperature.

### Table 2. Crystallographic data of samples 9–12, including lattice parameters of $\lambda$-Ti$_3$O$_5$ obtained by Rietveld refinement of the powder XRD patterns.

| Sample | 9 | 10 | 11 | 12 |
|--------|---|----|----|----|
| Sintering temperature (°C) | 1163 | 1163 | 1163 | 1163 |
| $\mathrm{H}_2$ flow rate (L min$^{-1}$) | 0.05 | 0.3 | 1.5 | 3.0 |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | $C2/m$ | $C2/m$ | $C2/m$ | $C2/m$ |
| $a$ (Å) | 9.883(17) | 9.820(2) | 9.791(3) | 9.794(5) |
| $b$ (Å) | 3.791(5) | 3.7912(5) | 3.7874(5) | 3.7767(9) |
| $c$ (Å) | 9.924(16) | 9.980(2) | 9.962(2) | 9.949(4) |
| $\beta$ (°) | 90.72(12) | 91.068(18) | 90.895(18) | 90.67(4) |
| $V$ (Å$^3$) | 369.4(10) | 371.49(12) | 369.37(14) | 368.0(3) |
| $Z$ | 4 | 4 | 4 | 4 |
| $R_{wp}$ (%) | 2.22 | 2.16 | 2.49 | 3.47 |
| $S$ | 1.2584 | 1.1775 | 1.2775 | 1.7190 |
| $\lambda$-Ti$_3$O$_5$ (%) | 10.4(5) | 100 | 79.5(5) | 62.9(11) |
| Anatase TiO$_2$ (%) | 89.6(6) | 0 | 0 | 0 |
| Impurity (Ti$_2$O$_3$) (%) | 0 | 0 | 20.5(3) | 37.1(9) |

#### 3.3. Temperature dependence of crystal structure

Variable-temperature XRD measurements were conducted for the $\lambda$-Ti$_3$O$_5$ nanocrystals. Figure 6 plots the peak position versus temperature for the XRD patterns of sample 10 measured in the range of 31.4–33.5°.

**Figure 6.** Peak position versus temperature of the XRD patterns in the angle range of 31.4–33.5° for sample 10. Diffraction peaks of $\lambda$-Ti$_3$O$_5$ (2 0 -3) and (2 0 3) (filled circles) change into the $\alpha$-Ti$_3$O$_5$ (0 2 3) peak (open circles) as the temperature increases.
33.5°. Upon heating, the diffraction peaks of $\lambda$-Ti$_3$O$_5$ transform into the $\alpha$-Ti$_3$O$_5$ peak with an orthorhombic crystal structure ($Cmcm$), e.g., (2 0 $-3$) and (2 0 3) $\lambda$-Ti$_3$O$_5$ peaks transform into the (0 2 3) $\alpha$-Ti$_3$O$_5$ peak around 500 K. Cooling to 300 K restores $\lambda$-Ti$_3$O$_5$. The observed phase transition temperature of 500 K is consistent with the reported second-order phase transition temperature between $\lambda$-Ti$_3$O$_5$ and $\alpha$-Ti$_3$O$_5$ for nanocrystals obtained by a combination of reverse–micelle and sol–gel techniques [20].

3.4. Mechanism

Next, we considered the reason why $\lambda$-Ti$_3$O$_5$ forms as nanocrystals by this sol–gel synthesis. In this method, the precursor Ti(OH)$_4$ particles are uniformly dispersed in the aqueous solution. The hydrolysis of TEOS into SiO$_2$ occurs slowly and homogeneously in the sol–gel process, resulting in a homogeneous SiO$_2$ shell over the precursor particle surfaces. Due to the SiO$_2$ matrix, the sintering process suppresses crystalline growth. Consequently, a combination of the sol–gel method and sintering process is suitable to form $\lambda$-Ti$_3$O$_5$ in the size of ca. ten nanometers. Furthermore, the dependence of the crystal size on temperature is due to the viscosity of the SiO$_2$ matrix; the viscosity of SiO$_2$ increases as the temperature decreases, which results in smaller nanocrystals at lower temperature.

4. Conclusion

Synthesizing small-sized nanocrystals of a photo-induced phase transition material is a promising method to develop high-density recording media. Herein we demonstrate that tuning the sintering temperature can control the size of the $\lambda$-Ti$_3$O$_5$ nanocrystals. A sintering temperature of 1123°C gives the smallest $\lambda$-Ti$_3$O$_5$ nanocrystals, 8 nm. Adjusting the hydrogen flow rate can tune the oxidation-reduction state of the sample without apparent change in the crystal size. The memory density in the recording media is estimated to be 1 terabit inch$^{-2}$ with nanocrystal size of 21 nm, which is our previously reported crystal size [20], while the density is expected to achieve 10 terabit inch$^{-2}$ with 8 nm nanocrystals. Although we prepared the smallest sized $\lambda$-Ti$_3$O$_5$ nanocrystals in this work, a study to synthesize even smaller nanocrystals is currently underway.

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