Formation of La$_2$Ti$_2$O$_7$ Crystals from Amorphous La$_2$O$_3$-TiO$_2$ Powders Synthesized by the Polymerized Complex Method

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Abstract−Amorphous La$_2$O-TiO$_2$ powders were synthesized by the polymerized complex (PC) method. The activation energies for crystallization and grain growth of La$_2$Ti$_2$O$_7$ from these precursors were determined from results of XRD and DTA and compared with those for La$_2$Ti$_2$O$_7$ precursors by the conventional solid-state reaction (SSR). Activation energy of grain growth of La$_2$Ti$_2$O$_7$ in PC-sample was determined to be 7.1 kJ/mol while that of SSR sample was 14.8 kJ/mol. The energy required for the phase transformation from amorphous PC sample to layered perovskite was 432 kJ/mol, while the SSR sample did not show this transition below 900 °C. It was clearly demonstrated that the La$_2$Ti$_2$O$_7$ crystals were formed at a lower temperature and they grew in size faster in the sample prepared by the PC method relative to the sample prepared by the SSR method. Mixing of elements in molecular level in PC preparation appeared responsible for these differences.

Key words: Photocatalytic Water Splitting, Polymerized Complex Method, Layered Perovskite Materials, Activation Energy, Crystallization, Grain Growth

INTRODUCTION

Among various methods of solar energy conversion [Ismagilov et al., 2003; Moon et al., 2002; Yang et al., 2002], photocatalytic splitting of water into H$_2$ and O$_2$ has received the most attention because of its potential to obtain directly clean and high-energy containing H$_2$ from abundant H$_2$O. Perovskite-type oxide materials based on transition metals with d(0) electron configuration such as Nb (V), Ta (V) and Ti (IV) have been investigated as efficient photocatalysts for overall water splitting [Domen et al., 1986, 2001; Inoue et al., 1994; Kudo and Kato, 1997; Reddy et al., 2003; Kim et al., 1999; Hwang et al., 2000]. These photocatalysts have been prepared by the conventional solid-state reaction (SSR), in which appropriate amounts of precursor oxides or carbonates are ground together and then calcined at high temperatures (>1,000 °C) for long hours to allow interdiffusion of cations. This preparation method produces materials of low surface areas, nonuniform particle sizes and low phase purity. If perovskite-type oxide materials could be prepared by using a low-temperature synthetic route, it might be possible to enhance the BET surface area of perovskite-type oxide materials, and thus to increase the photocatalytic activity for water decomposition.

An improved synthesis method is in order that gives active photocatalysts with high surface areas [Kakihana and Yoshimura, 1999]. The polymerizable complex (PC) method has been widely used to prepare multi-component oxides at low temperatures. Indeed, K$_2$La$_2$Ti$_3$O$_{10}$ prepared by the polymerized complex method was reported to have a high surface area due to the low temperature heat-treatment, and also to exhibit much higher activity than photocatalysts prepared by the conventional SSR method [Ikeda et al., 1998]. We

have also succeeded in fabricating highly donor-doped (110) layered perovskite materials, La$_2$Ti$_2$O$_7$, by the PC method and found that the quantum yield of the reaction over La$_2$Ti$_2$O$_7$ prepared by the PC method was as high as 27%, which is about two-fold greater than that over La$_2$Ti$_2$O$_7$ prepared by the SSR method for photocatalytic water decomposition under ultraviolet (UV) irradiation. La$_2$Ti$_2$O$_7$ prepared by the PC method showed higher surface areas, higher phase purity and more uniform morphology than those of La$_2$Ti$_2$O$_7$ prepared by the SSR method [Kim et al., 2003].

Although it was demonstrated that product crystals in samples prepared by the PC method were formed at a temperature lower than the temperature needed for the SSR method, more quantitative investigation of the crystallization process is needed to understand the reason for the reduction in the processing temperature and to develop photocatalysts with desired high crystallinity and surface areas. In the present study, formation kinetics and crystallization behaviors of La$_2$Ti$_2$O$_7$ in amorphous La$_2$O-TiO$_2$ powders prepared by the PC method were investigated by using X-ray diffraction (XRD) and differential thermal analysis (DTA). The activation energies for crystallization and grain growth of La$_2$Ti$_2$O$_7$ were obtained from these data. Qualitative crystallization behavior was also confirmed by scanning electron microscopy (SEM) and high-resolution electron microscopy (HR-TEM).

EXPERIMENTAL

1. Sample Powders Preparation

Fig. 1 shows a flowchart of the synthesis procedure for La$_2$Ti$_2$O$_7$ crystals by the PC method. Titanium isoproxide (Ti(OCH(CH$_3$)$_2$)$_4$, 99.0%, Aldrich), ethylene glycol (C$_2$H$_6$O$_2$, Kanto Chemicals), citric acid (C$_6$H$_8$O$_7$, Wako) and lanthanum nitrate hydrate (La(NO$_3$)$_3$·6H$_2$O, 99.99%, Aldrich) were used as starting materials. After titanium isoproxide was dissolved into ethylene glycol, an appropriate

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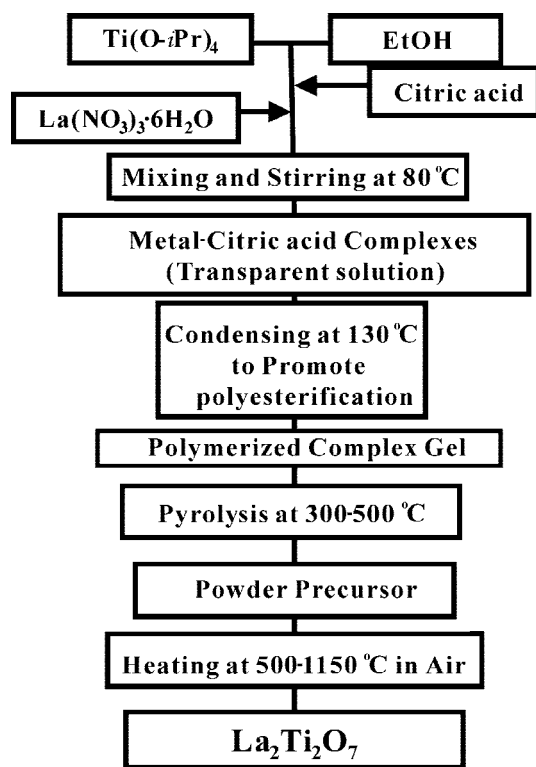[†]To whom correspondence should be addressed.
E-mail: jlee@postech.ac.kr

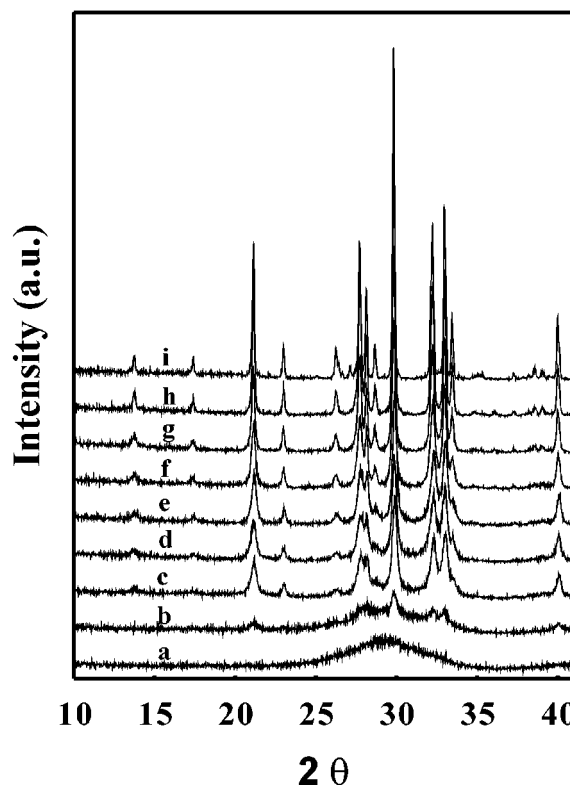Fig. 1. A flowchart for preparing La$_2$Ti$_2$O$_7$ by the polymerized complex method.

Fig. 2. XRD patterns of (a) a precursor sample prepared by the PC method, and of La$_2$Ti$_2$O$_7$ formed in the precursor PC-samples heat-treated at (b) 650 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C, (f) 950 °C, (g) 1,000 °C, (h) 1,050 °C.

amount of anhydrous citric acid was added to convert Ti(OCH(CH$_3$)$_2$)$_4$ to stable Ti-citric acid complexes, and then a methanol solution containing La(NO$_3$)$_3$·6H$_2$O was finally added. This solution was heated on a hot plate at 80 °C, until it became a transparent colorless solution. The solution was heated at 130 °C for several hours to obtain a polymeric gel. The viscous polymeric product was pyrolyzed at about 300-500 °C to form precursor powders. The powder precursor was pressed in the form of pellets, which were calcined at 500-1,150 °C for 2 h in an electric furnace to obtain crystalline La$_2$Ti$_2$O$_7$. On the other hand, for the purpose of comparison, La$_2$Ti$_2$O$_7$ was also prepared by the conventional solid-state reaction (SSR) method. Crystalline La$_2$Ti$_2$O$_7$ powders were formed by heating a ground mixture of La$_2$O$_3$ (99%, Aldrich) and TiO$_2$ (99%, Aldrich) at 1,000, 1,050, 1,100, and 1,150 °C, respectively.

2. Characterization

The La$_2$Ti$_2$O$_7$ crystals in the samples prepared by the PC and conventional SSR methods were characterized by XRD (Mac Science Co., M18XHF). XRD peaks were compared with data from the Joint Committee Powder Diffraction Standards (JCPDS) for identification of the formed phase. The morphology was determined by scanning electron microscopy (SEM, Hitachi, S-2460N) and high-resolution transmission electron microscopy (HR-TEM, Philips, CM 200). Differential thermal analyses (Shimadzu, DTA-50) were carried out at the temperature range 30-900 °C with the various heating rates of 5, 10, 15, 20 and 30 °C/min.

RESULTS AND DISCUSSION

1. Crystallization Behavior of La$_2$Ti$_2$O$_7$

In order to compare crystallization behaviors of PC and SSR samples, their powder XRD patterns are shown in Fig. 2. In the case of sample (i) prepared by the SSR method at 1,150 °C, only XRD peaks attributable to La$_2$Ti$_2$O$_7$ phase are observed. The XRD patterns for the PC precursor sample (a) and the PC samples heat-treated below 650 °C were primarily those of amorphous solids, indicating that the PC precursor sample was not crystallized at such low temperatures. The presence of both La$_2$Ti$_2$O$_7$ and amorphous phases in PC sample heat-treated at 700 °C was detected by XRD. A broad continuum around 25-35°, indicative of the presence of an amorphous phase, persisted even after the calcination temperature was raised from 700 °C to 850 °C. However, all XRD reflections of the PC sample heat-treated above 900 °C exhibited a single phase of La$_2$Ti$_2$O$_7$. XRD patterns of the PC samples heat-treated above 900 °C were almost the same as that of the SSR sample. This result indicates that the crystallization of La$_2$Ti$_2$O$_7$ in PC sample is completed between 900 °C and 1,050 °C. The lattice parameters of La$_2$Ti$_2$O$_7$ in Fig. 2(e-i) were estimated to be a=7.8 Å, b=13.015 Å, c=5.546, γ= 98.64 (JCPDS-28-517). The crystal structure of La$_2$Ti$_2$O$_7$ phase is built up of layers of distorted perovskite-like slabs running parallel to the (110) plane. The thickness of the slabs corresponds approximately to four corner-linked (TiO$_6$)$^{8-}$ octahedral.

2. SEM and TEM Micrographs of La$_2$Ti$_2$O$_7$

Fig. 3 shows SEM photographs for La$_2$Ti$_2$O$_7$ crystals prepared by the PC method (A, B and C) and the SSR method (D, E and F). The growth of La$_2$Ti$_2$O$_7$ particles in PC samples and SSR samples was different. The PC sample prepared at a low sintering tempera-
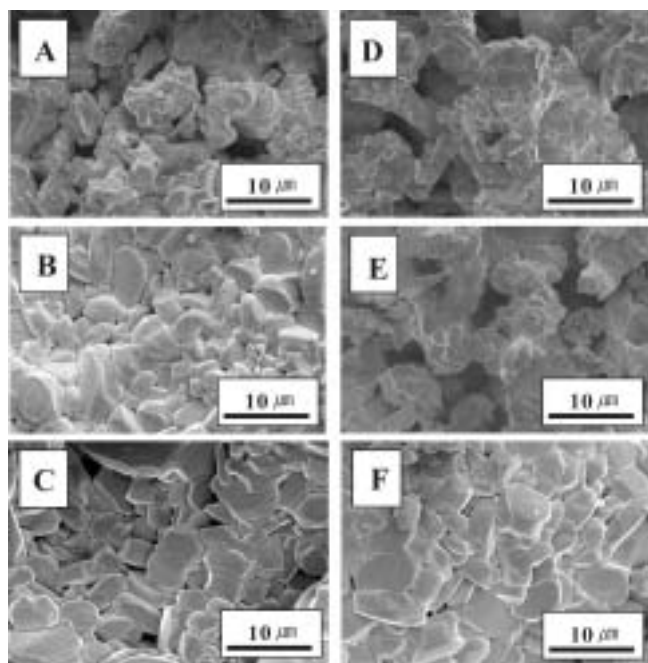
Fig. 3. SEM photographs for the growth of La₂Ti₂O₇ crystal prepared by the PC method at (A) 1,000 °C, (B) 1,050 °C, (C) 1,100 °C and by the SSR method at (D) 1,050 °C, (E) 1,100 °C, (F) 1,150 °C.

ture of 1,000 (A) consists of particles that form agglomerates of 1-2 μm. When the sintering temperature increased to 1,050 (B) and 1,100 °C (C), La₂Ti₂O₇ crystals showed large and well-developed particle morphology. The particle sizes of PC sample increased with increasing calcination temperatures. However, in case of SSR samples (D, E and F), the crystallization behavior and particle morphology of La₂Ti₂O₇ were different from those of PC samples. Thus, SSR samples (D and E) were prepared at higher temperatures (1,050 °C and 1,100 °C, respectively) than that for the PC sample (A), but a crystalline La₂Ti₂O₇ phase was not complete grown in the SSR samples (D and E). A morphology indicating complete crystallization was observed for the SSR sample treated at 1,150 °C. Thus, in the La₂Ti₂O₇ formation, the temperature difference for complete crystallization between the PC method and SSR method was about 100 °C.

If the La₂Ti₂O₇ in PC and SSR samples showed good crystallinity, a layered structure of La₂Ti₂O₇ could be observed by HR-TEM [Bowden et al., 1995]. Fig. 4 shows HR-TEM images of the precursor sample (A), the heat-treated PC sample at 1,050 °C (B) and SSR sample prepared at 1,150 °C (C). The precursor powders (A) consist of fine particles that form agglomerates of 1-2 nm in size and are not yet crystallized. However, the HR-TEM image for both samples (B and C) shows a layered structure of La₂Ti₂O₇ with a layer thickness of 10.57 Å and an interlayer spacing of 2.48 Å as expected from its lattice parameters. Although PC sample (B) and SSR sample (C) were prepared at different sintering temperatures, La₂Ti₂O₇ in both samples showed the same good crystallinity as shown in Figs. 3 and 4.

3. Crystallite Size and Activation Energies of Grain Growth of La₂Ti₂O₇

The crystallite size of the La₂Ti₂O₇ formed in heat-treated PC sam-

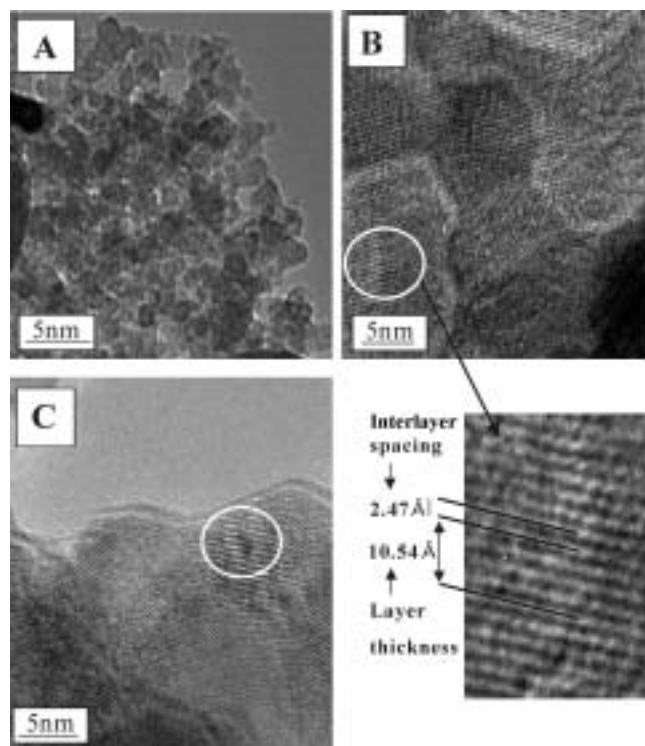**Fig. 4. TEM images of (A) a precursor sample prepared by the PC method, and of La₂Ti₂O₇ formed in the precursor PC-samples heat-treated at (B) 1,050 °C, and of La₂Ti₂O₇ prepared by the SSR method at (C) 1,150 °C.**

ple was estimated from the full width at half maximum intensity (FWHM) of an XRD peak (Fig. 2) by using Scherrer's equation [Cullity, 1978] as shown below;

$$L=0.9\lambda/B\cos\theta \quad\quad\quad (1)$$

where λ is the wavelength of X-ray radiation (λ=0.154 nm), B is

Table 1. The relationship between density (g/cm³) and crystallite size (nm) of Li₂Ti₂O₇ prepared by PC sample (PC samples heat-treated at various temperatures) and SSR method

Catalyst	Temperature (°C)	Crystallite size (nm)	Density (g/cm³)
PC sample	700	42.2	4.2
PC sample	750	44.8	4.51
PC sample	800	44.8	4.57
PC sample	850	47.1	4.92
PC sample	900	51.2	5.44
PC sample	950	51.2	5.51
PC sample	1,000	55.2	5.68
PC sample	1,050	55.4	5.70
PC sample	1,100	55.6	5.71
PC sample	1,150	55.6	5.73
SSR sample	1,000	55.1	5.65
SSR sample	1,050	56.2	5.67
SSR sample	1,100	57.8	5.69
SSR sample	1,150	59.7	5.71

FWHM of the peak (radians) corrected for instrumental broadening, θ is Bragg angle, and L is the crystallite size (Å). Crystallite size and density for the heat-treated PC samples and SSR samples are given in Table 1. The density and crystallite size of PC sample and SSR sample increased rapidly with increasing heat treatment temperatures. At the same calcination temperatures, crystallite size and density of both the PC and SSR samples were similar.

The activation energy required for grain growth of La₂Ti₂O₇ crystal in PC sample and SSR sample could be estimated by the Arrhenius plot of the results shown in Table 1. According to Coble's theory [Coble, 1961], the activation energy of grain growth can be calculated by the Arrhenius equation:

$$d \ln k/dT = E/RT^2, \tag{2}$$

where k is the specific reaction rate constant, E is the activation energy, T is the absolute temperature and R is the ideal gas constant.

Jarcho et al. [1976] discovered the value of k was related to the grain size directly. Thus, modification and integration Eq. (2) becomes

$$\log D = (-E/2.303R)/T + A, \tag{3}$$

where D is the grain size and A is the intercept.

From a plot of log D versus the reciprocal of absolute temperature (1/T) from Eq. (3), one obtains a straight-line as shown in Figs. 5 and 6. The slope of the line gives the activation energy of grain growth of La₂Ti₂O₇ in the PC and SSR samples. Activation energies of grain growth of La₂Ti₂O₇ were determined to be 7.1 kJ/mol for the PC sample and 14.8 kJ/mol for the SSR sample, respectively. Thus, the SSR method has a higher activation energy of crystal growth by a factor of ca. 2 compared to the PC method. The most significant difference in crystallization processes between PC and SSR methods is the state of their precursors, and thus the species involved in the crystal growth process.

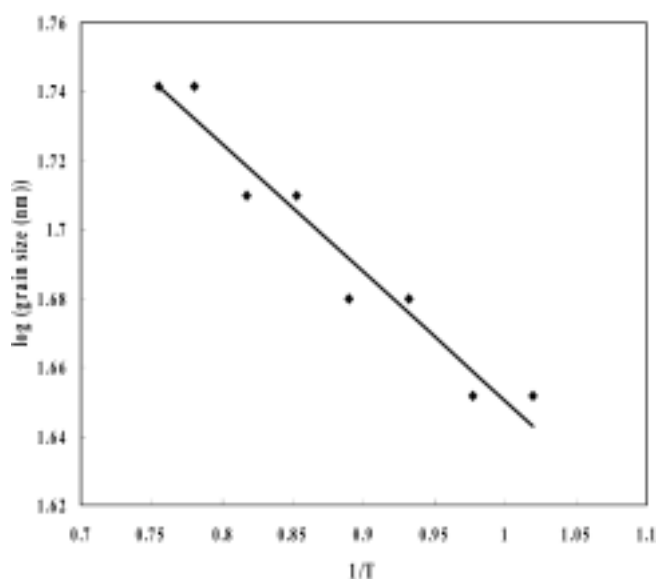The solid state reactions between fine particles of La₂O₃ and TiO₂

Fig. 6. A plot of log(grain size of La₂Ti₂O₇ prepared by the SSR method at 1,000 °C, 1,050 °C, 1,100 °C and 1,150 °C) versus the reciprocal of absolute temperature (1/T)×1,000.

require heat treatment at relatively high temperatures (>1,100 °C) to obtain an La₂Ti₂O₇ phase. However, PC synthesis involves mixing of elements at a molecular level and the diffusion path length is reduced to nanometer scale for obtaining the desired material. As a consequence, the PC method needs lower temperatures and a lower activation energy to obtain crystalline phase than the SSR method.

4. La₂Ti₂O₇ Formation Kinetics in PC Sample by DTA Analysis

Fig. 5. A plot of log(grain size of La₂Ti₂O₇ formed in the PC sample heat-treated at various temperatures) versus the reciprocal of absolute temperature (1/T)×1,000.
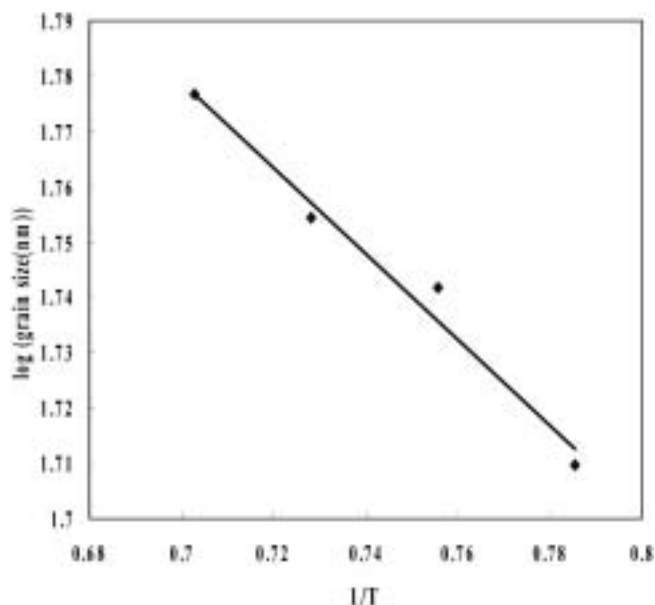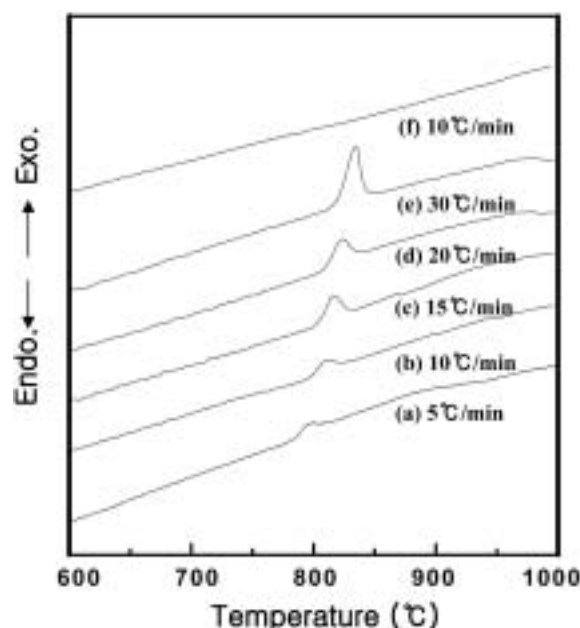

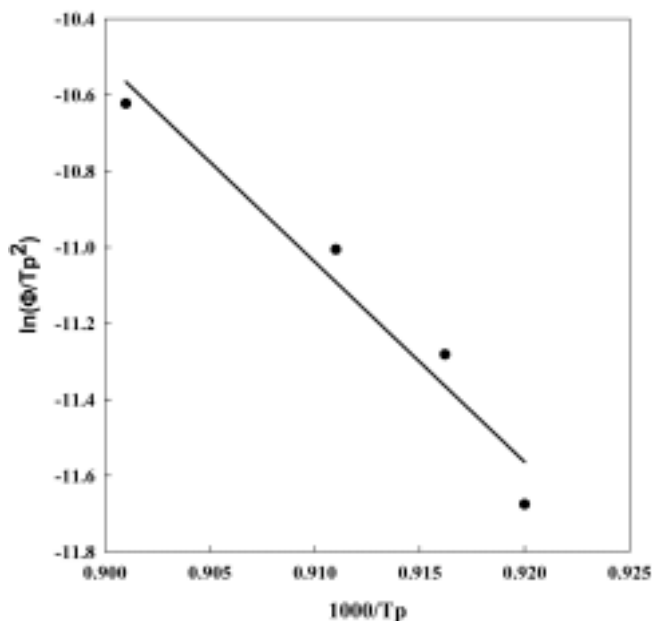Fig. 7. DTA curves of a precursor sample prepared by the PC method (a-e) and of La₂Ti₂O₇ prepared by the SSR method (f).

Fig. 8. A plot to obtain the activation energy involved in the amorphous to crystallization La$_2$Ti$_2$O$_7$ transformation of PC sample.

Thermal behaviors of both the PC sample and SSR sample were investigated by differential thermal analyses (DTA). Fig. 7 shows DTA patterns for the amorphous PC sample in the temperature range of 50-900 °C with different heating rates of 5, 10, 15, 20 and 30 °C/min. At a heating rate of 10 °C/min, an exothermic peak of PC sample was observed at around 772 °C and the peak shifts to high temperatures with increasing heating rates (15, 20 and 30 °C/min) for the amorphous PC sample. In the case of SSR sample, however, the exothermic or endothermic peaks are not observed in the temperatures range of 50-900 °C. The results of DTA analysis for PC sample, in which crystallization of La$_2$Ti$_2$O$_7$ in PC sample begins at around 772 °C, are in good accordance with XRD analysis as shown in Fig. 2(c).

The energy for crystallization of La$_2$Ti$_2$O$_7$ in PC sample could be calculated from the different heating rates and the exothermic peak temperature values in Fig. 4 using the Kissinger's or Redhead's equations as follows [Kissinger, 1956; Redhead, 1962]:

$$\ln(\varPhi/T_p^2) = -E/RT_p + const. \tag{4}$$

where $\varPhi$ is heating rate, T$_p$ is the peak temperature, R is the ideal gas constant. As shown in Fig. 8, the plot of $\ln(\varPhi/T_p^2)$ vs. (1000/T$_p$) for the PC sample showed a straight line. The energy required for the phase transformation from amorphous PC sample to layered perovskite, La$_2$Ti$_2$O$_7$, was calculated to be 436.8 kJ/mol from the slope of the straight line. The activity of water-splitting reaction showed a maximum for the sample prepared at a temperature where the crystallinity and surface area of La$_2$Ti$_2$O$_7$ were optimized [Kim et al., 2003]. Thus, the obtained energy required for crystallization in amorphous PC sample is one of the important factors to consider for fabricating La$_2$Ti$_2$O$_7$ photocatalyst with a high photocatalytic activity for photocatalytic water decomposition. In the case of the samples prepared by the SSR-method, phase transition of La$_2$Ti$_2$O$_7$ was not observed below 900 °C as shown in Fig. 7(f).

For the formation of La$_2$Ti$_2$O$_7$ layered perovskite, the activation energies of PC and SSR samples are closely related to the state of the starting precursors. Thus, the PC precursor sample consists of the random O-La-O-Ti-O network with nanometer scale, but the SSR sample is made of micro size particles of the binary oxides (La$_2$O$_3$ and TiO$_2$). Thus, La$_2$Ti$_2$O$_7$ synthesis by SSR method requires high temperatures because La$_2$Ti$_2$O$_7$ is formed by cation diffusion in the range of micrometers in contrast to the nanometer scale movement required for PC samples. Therefore, La$_2$Ti$_2$O$_7$ crystals in samples prepared by the PC method were formed at a temperature lower than the temperature needed for the SSR method.

CONCLUSION

Amorphous La$_2$O-TiO$_2$ powders were prepared by the polymerized complex (PC) method and the crystallization kinetics of La$_2$Ti$_2$O$_7$ was investigated by using XRD and DTA. The activation energy of grain growth of La$_2$Ti$_2$O$_7$ in the PC-sample was lower than that of the SSR sample by a factor of ca.2. The crystallization of La$_2$Ti$_2$O$_7$ phase in the PC sample occurs at least 100 °C lower temperature than for the SSR sample. The reason for the reduction in the processing temperature and activation energy of crystallization of the PC sample can be attributed to mixing of elements at a molecular level in PC synthesis, which would facilitate diffusion process during the crystal growth. The energy for the phase transformation from amorphous PC-sample to layered perovskite was determined to be 432 kJ/mol.

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