

Formation of Layered  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  Perovskite in  $\text{Bi}_2\text{O}_3$ - $\text{TiO}_2$ - $\text{Fe}_2\text{O}_3$  Containing System

Pramod H. Borse,<sup>†,§</sup> Sang Su Yoon,<sup>‡</sup> Jum Suk Jang,<sup>§</sup> Jae Sung Lee,<sup>§</sup> Tae Eun Hong,<sup>#</sup> Euh Duck Jeong,<sup>#</sup>  
Mi Sook Won,<sup>#</sup> Ok-Sang Jung,<sup>‡</sup> Yoon Bo Shim,<sup>‡</sup> and Hyun Gyu Kim<sup>\*,\*</sup>

<sup>†</sup>Center for Nanomaterials, International Advanced Research Center for Powder Metallurgy and New Materials (ARC International), Balapur PO, Hyderabad. AP. 500 005, India

<sup>‡</sup>Department of Chemistry (BK21), Pusan National University, Busan 627-706, Korea

<sup>§</sup>Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea

<sup>#</sup>Busan Center, Korea Basic Science Institute, Busan 609-735, Korea. \*E-mail: hhgkim@kbsi.re.kr

Received September 3, 2009, Accepted October 20, 2009

Structural and thermo-analytical studies were carried out to understand the phase formation kinetics of the single phase  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  (BTFO) nanocrystals in  $\text{Bi}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$ , during the polymerized complex (PC) synthesis method. The crystallization of Aurivillius phase  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  layered perovskite was found to be initiated and achieved under the temperature conditions in the range of  $\sim 800$  to  $1050$  °C. The activation energy for grain growth of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  nanocrystals (NCs) was very low in case of NCs formed by PC (2.61 kJ/mol) than that formed by the solid state reaction (SSR) method (10.9 kJ/mol). The energy involved in the phase transformation of Aurivillius phase  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  from  $\text{Bi}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  system was  $\sim 69.8$  kJ/mol. The formation kinetics study of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  synthesized by SSR and PC methods would not only render a large impact in the nanocrystalline material development but also in achieving highly efficient visible photocatalysts.

**Key Words:**  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ , Aurivillius phase, Polymerized complex method, Activation energy, Crystallization behavior

### Introduction

The remarkable progress of photocatalysis in last decade was limited to ultraviolet (UV) light region although the visible light is far more abundant and useful for an efficient photocatalysis under solar light. Thus the development of the visible light photocatalysts has become an important topic in the photocatalysis research today. To date, several research groups have developed visible active photocatalysts of oxide, sulfide, oxy-nitride such as  $\text{PbBi}_2\text{Nb}_2\text{O}_9$ ,  $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ , Zr-S co-doped  $\text{TiO}_2$ ,  $\text{Ni}_x\text{In}_{1-x}\text{TaO}_4$ ,  $\text{TaON}$ ,  $\text{TiO}_{2-x}\text{N}_x$ ,  $\text{TiO}_{2-x}\text{C}_x$ , and  $\text{AgGa}_{1-x}\text{In}_x\text{S}_2$ , etc.<sup>1-9</sup> In search of the highly efficient photocatalysts under visible light irradiation, we have recently discovered a novel single oxide photocatalysts,  $\text{PbBi}_2\text{Nb}_2\text{O}_9$ , with an Aurivillius-phase perovskite as well as nanocomposite and p-n junction nanodiode, etc.<sup>10-14</sup> But, we still need highly efficient, small band gap (ca. 1.9 ~ 2.1 eV) photocatalyst which will efficiently absorbs the visible light photons from the solar spectrum.

Recently, Sun *et al.* reported that  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  showed a significant photocatalytic activity for the decomposition of the Rhodamine B and acetaldehyde under visible light irradiation.<sup>15</sup> They synthesized  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  using a high pressure synthesis. We have also succeeded in fabricating a layered perovskite phase of the Aurivillius phase,  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ , by the polymerized complex (PC) method and found that the photocatalytic activity of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  nanocrystalline was much higher than that of  $\text{TiO}_{2-x}\text{N}_x$  for IPA photodegradation and hydrogen production under visible light ( $\lambda \geq 420$  nm). It is important to note that the conditions required for the crystallization and ultimately desired phase formation of pure nanocrystalline  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  are very different in each method. Thus the present work on the

formation kinetics of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  made by different methods is very important thus enable one to optimize the crystal structure and particles size of visible light active photocatalyst.

In the present study, the thermal properties and formation kinetics of single phase  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  crystals in  $\text{Bi}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  synthesized by polymerized complex method were investigated using differential thermal analysis and X-ray diffraction and further compared with  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  crystals made by solid state reaction (SSR) method. The activation energies for the grain growth and the crystallization of single  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  in  $\text{Bi}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  were obtained from these data. We also investigated the particle morphology and a layered structure of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  by scanning electron microscopy and high-resolution electron microscopy.

### Experimental

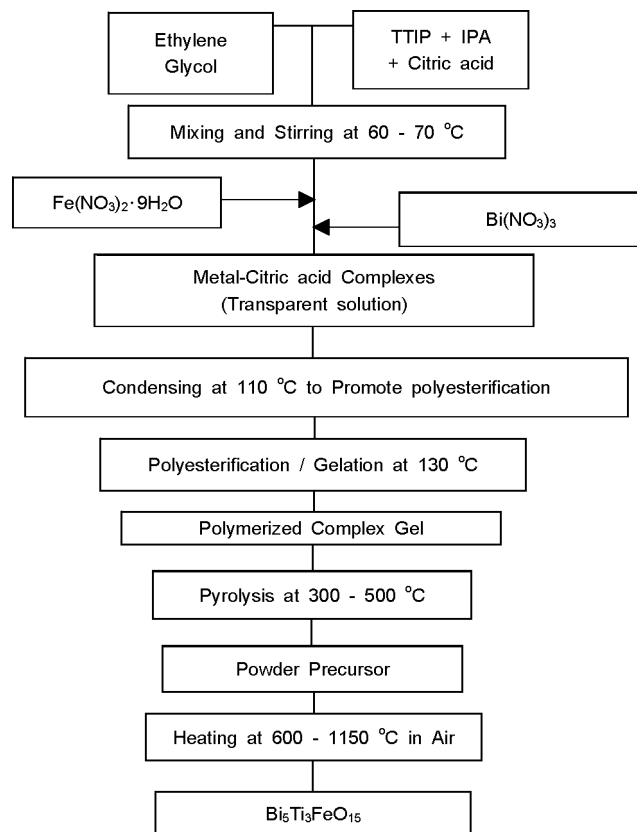
Nanocrystalline  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  was synthesized by the PC method according to the procedure in described in our previous work.<sup>16,17</sup> Bismuth nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , 99.5%, Aldrich), iron nitrate hydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 98%, Aldrich), titanium(IV) isopropoxide ( $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ , 97%, Aldrich), ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ , Kanto Chemicals) and citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ , Wako) were used as starting materials, under constant agitation, at the temperature of 60 - 70 °C. Next, the titanium isopropoxide dissolved in isopropyl alcohol (IPA) solution was added in CA-EG solution to obtain Ti-citrate complex. Finally, the salts of bismuth nitrate pentahydrate and iron nitrate hydrate were added and dissolved in Ti-citrate complex solution. The mixture was kept on hot plate (70 °C) till it became a transparent colorless solution. The colorless solution was condensed at 110 °C to promote the polyesterification and then 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 the precursor powders. Thus the powder obtained was pressed in the form of pellets, which were calcined in range temperature range of 650 - 1100 °C for 4 h in an electric furnace to obtain the nanocrystalline  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ . The schematic procedure of synthesis of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  by polymer complex method is shown in Figure 1. On the other hand, for the purpose of the comparison,  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  was also prepared by the conventional SSR method. Crystalline  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  powders were formed by heating a ground mixture of  $\text{Bi}_2\text{O}_3$  (99%, Aldrich),  $\text{TiO}_2$  (99%, Aldrich) and  $\text{Fe}_2\text{O}_3$  (99%, Aldrich) at 800 - 1100 °C for 4 h, respectively.

The  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  samples prepared by the PC were characterized by X-ray Diffractometer (Mac Science Co., M18XHF). X-ray diffraction (XRD) results were compared with the Joint Committee Powder Diffraction Standards (JCPDS) data for phase identification. The glass transition,  $T_g$  and crystallization peak,  $T_x$ , temperatures were determined using differential thermal analysis (Shimadzu, DTA-50).<sup>18</sup> DTA were carried out at in the temperature range of 30 - 1000 °C with various heating rates of 10, 20, 30 and 40 °C/min. The morphology was determined by scanning electron microscopy (SEM, Hitachi, S-2460N).

## Results and Discussion

Structural characterization of SSR and PC samples were carried out to analyze and compare the crystallization behavior



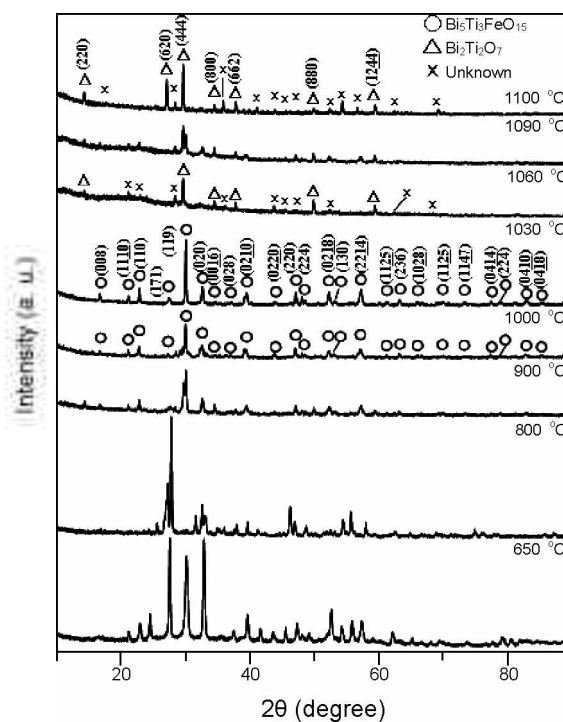
**Figure 1.** A schematic of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  synthesis followed in the polymer complex method.

of the samples prepared at various calcination temperatures. Figure 2 and 3 show the XRD patterns of SSR and PC samples, respectively. It is evident from Figure 2 that the temperature (1030 °C) of formation of single phase of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  was crucial in case of samples made by SSR method. Moreover the Aurivillius phase of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  was not retained at the temperature around 1060 °C. Evidently it can be observed that the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  cannot be formed at temperature lower than 1030 °C, a different impurity phase is observed at the temperature above 1060 °C. On the contrary in case of samples made by PC method, the initiation and formation of Aurivillius  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  structure was found to occur in the temperature range of 800 to 1030 °C. This indicated that  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  could be crystallized at such low temperatures (~800 °C) without any impurity phases unlike to the SSR samples. The PC sample did display similar behavior to that of SSR, in which the samples exhibited  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase only upto 1030 °C and no pure  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase was observed at 1060 °C. The lattice parameters of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  were estimated to be  $a = 5.45 \text{ \AA}$ ,  $b = 5.46 \text{ \AA}$ ,  $c = 41.2 \text{ \AA}$  (JCPDS). Thus the crystallization behavior of PC sample of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  was significantly different from that of SSR samples as shown in Figure 3.

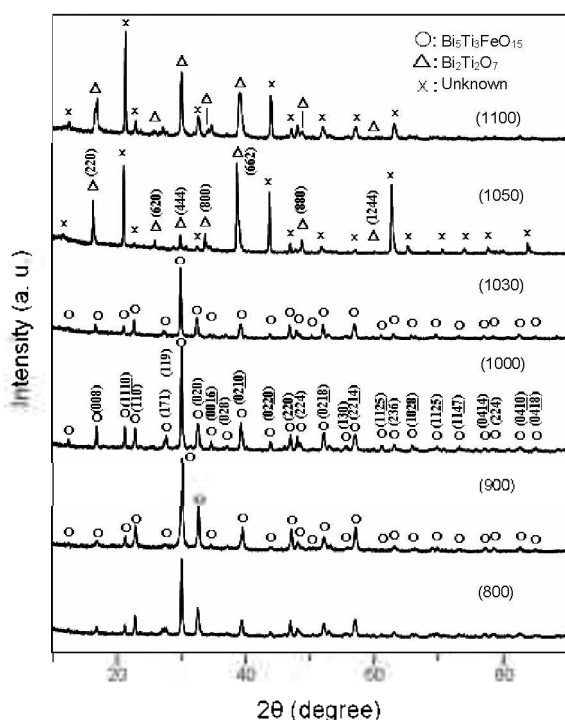
The crystallite size of the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  crystallites formed by SSR method (see Figure 2, a typical sample prepared at 1030 °C) and by PC method (see Figure 3, a typical sample prepared at 1030 °C) was estimated from the FWHM of main XRD peak by using the Scherrer's equation:<sup>19</sup>

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

Here  $\lambda$  is the wavelength of X-ray radiation ( $\lambda = 0.154 \text{ nm}$ ).



**Figure 2.** XRD patterns of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ -SSR samples calcined at (a) 650 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C, (e) 1030 °C, (f) 1060 °C, (g) 1090 °C, (h) 1100 °C, for 4 h.



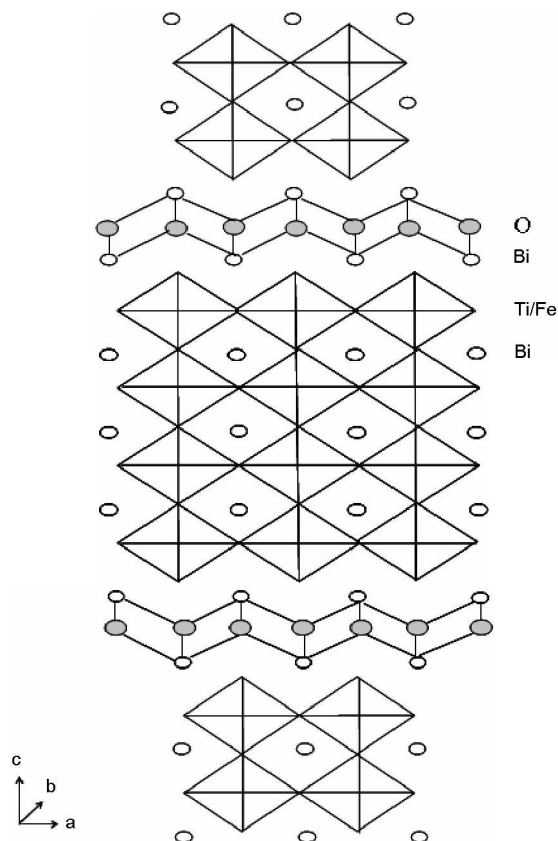
**Figure 3.** XRD patterns of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ -PC samples calcined at (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1030 °C, (e) 1050 °C, (f) 1100 °C, for 4 h.

**Table 1.** The relationship between sintering temperature and crystallite size of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  prepared by PC and SSR method.

Material	Sintering Temperature (°C)	Crystal size (nm)
PC sample	800	26
PC sample	900	28
PC sample	1000	29
PC sample	1030	28
SSR sample	900	17
SSR sample	1000	15
SSR sample	1030	27

B is FWHM of the peak (in radians) corrected for instrumental broadening.  $\theta$  is Bragg angle, and D is the crystallite size (Å). The crystallite sizes for both the samples are nearly same lying in the range of 17 - 29 nm indicating that pure  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase particles have been formed under respective conditions. This demonstrates that a pure phase can be obtained at a relatively lower temperature in case of PC samples than SSR sample. Crystallite size for the calcined SSR and PC samples are given in Table 1. Crystallite size of PC sample was larger than that of SSR sample.

The crystal structure of Aurivillius phase layered perovskite  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  is shown in Figure 4.  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  has a general formula of  $[\text{Bi}_2\text{O}_2]^{2-}[\text{B}_{m-1}\text{M}_m\text{O}_{3m-1}]^{2-}$ , where B is the 12-fold coordinated cation with low valence in the perovskite sublattice. M denotes the octahedral site occupied by the ions with high valence, and  $m$  is the number of perovskite layers between the  $[\text{Bi}_2\text{O}_2]^{2-}$  layers.<sup>20,21</sup> The perovskite sheets of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  are composed of  $\text{MO}_6$  octahedrons and 12-fold coordinated  $\text{Bi}^{3+}$



**Figure 4.** The crystal structure of Layered perovskite  $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+5}$  Aurivillius phase with  $m = 4$ .

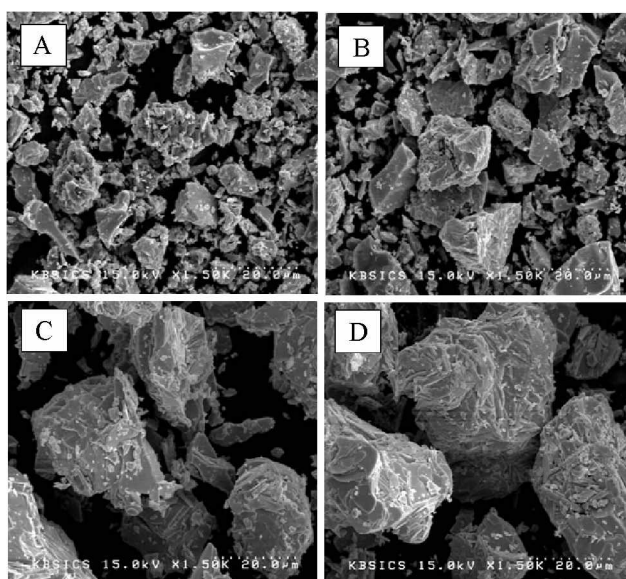
and are four layers in the thickness with the disordered  $\text{Ti}^{4+}$  to  $\text{Fe}^{3+}$  (3:1 ratio) in the M sites as shown in Figure 4.<sup>15</sup> Such layered structures are important in attaining a better efficiency than simple binary unlayered metal oxides.

Figure 5 shows SEM images of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  crystals prepared by PC method at various temperatures. The particle sizes of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  increased with the increasing calcination temperature. The crystallite sizes of PC samples estimated by the Scherrer's equation are in the range of 26 - 29 nm. The correlation of XRD and SEM studies indicates that the particles observed in SEM are the agglomerates of 26 - 29 nm crystallite size. Despite the similarity in the crystal sizes, it is seen that the average particle size for  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  formed in the PC sample is larger compared to those formed in the SSR sample. It is important to understand this observation in context to activation energy required for grain growth as described in following section below. These activation energies for the single phase  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  can be estimated by using the Arrhenius plot and crystal size of the samples shown in Table 1.

According to Coble's theory,<sup>22</sup> the activation energy for the grain growth can be calculated from the Arrhenius equation:

$$d \ln k/dT = E/RT^2 \quad (2)$$

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.*<sup>23</sup> discovered that the value of  $k$  was



**Figure 5.** SEM images of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  crystal prepared by (a) SSR (calcined at  $1030\text{ }^\circ\text{C}$ ), and (b) PC (calcined at  $1000\text{ }^\circ\text{C}$ ) method.

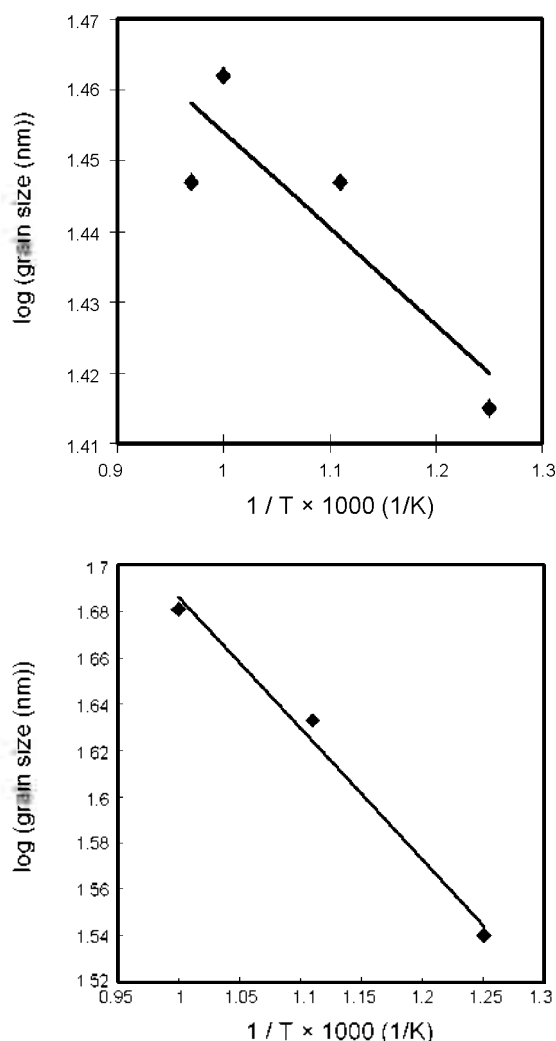
related with the grain size directly. Thus the modification and integration of Eq. (2) yields the grain size as:

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

where  $D$  is the grain size and  $A$  is intercept from the plot of  $\log D$  versus the reciprocal of absolute temperature ( $1/T$ ) from Eq. (3), as obtained as a straight-line in Figure 6. The slope of this line gives the activation energy for grain growth in the single phase  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  formed by  $\text{Bi}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-TiO}_2$  system in PC (Figure 6a) and SSR (Figure 6b) methods. The activation energy of the grain growth of the single phase  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  was estimated to be  $2.61\text{ kJ/mol}$  for PC sample and  $10.9\text{ kJ/mol}$  for SSR sample. This implies that in PC sample the i) particles are susceptible to grow faster than in SSR and ii) the phase transformation starts at much lower temperature as evident from the above analyses. Thus the above consideration is important for preparing the nanocrystalline  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ .

Further it is surprising to note that the occurrence of phase formation in PC and SSR samples is very different. Accordingly, nanocrystalline powders (PC sample) are ideal for phase transformation/crystallization studies, as ensemble of particles can be treated as an amorphous system. The thermal behaviors of Bi-Fe-Ti precursor powder (PC sample) were investigated by DTA. Figure 7 shows DTA patterns for the Bi-Fe-Ti precursor powder (PC sample) in the temperature range of  $200\text{ - }600\text{ }^\circ\text{C}$  for various heating rates of 10, 20, 30 and  $40\text{ K minute}^{-1}$ . At a heating rate of  $10\text{ }^\circ\text{C/min}$ , an exothermic peak of Bi-Fe-Ti precursor powder was observed at around  $416\text{ }^\circ\text{C}$ , and the peak shifted to the high temperatures with the increasing heating rates (20, 30 and  $40\text{ }^\circ\text{C/min}$ ). The respective values of the first exothermic peak for Bi-Fe-Ti precursor powders are given in Table 2.

The energy of formation of the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase in  $\text{Bi}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-TiO}_2$  containing precursor system may be calculated from crystallization onset temperature ( $T_x$ ) values in Table 2



**Figure 6.** A plot of  $\log(\text{grain size of } \text{Bi}_5\text{Ti}_3\text{FeO}_{15} \text{ formed in the } \text{Bi}_2\text{O}_3\text{-TiO}_2\text{-Fe}_2\text{O}_3 \text{ system heat-treated at various temperatures) versus the reciprocal of absolute temperature } (1/T) \times 1000\text{ K}^{-1}$  for (a) PC sample and (b) SSR sample.

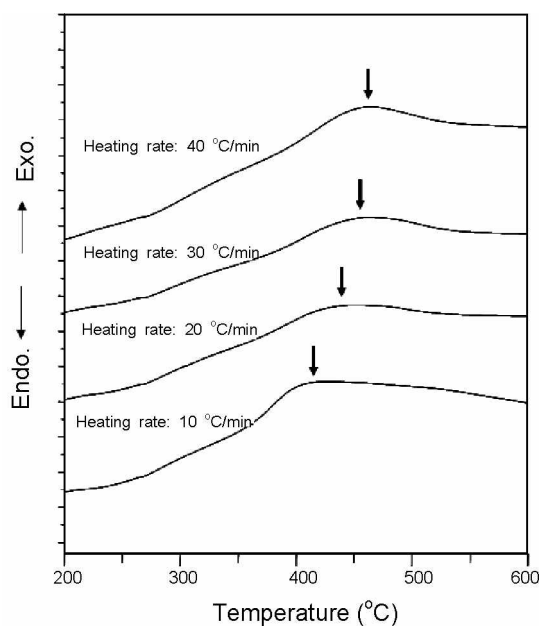
**Table 2.** Values of heating rate and exothermic temperature for  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  PC sample in the temperature range of  $200\text{ - }600\text{ }^\circ\text{C}$  with different heating rates.

Material	Heating rate ( $^\circ\text{C/min}$ )	Exothermic Temp. ( $^\circ\text{C}$ )
PC sample	10	416.04
PC sample	20	438.91
PC sample	30	452.50
PC sample	40	464.89

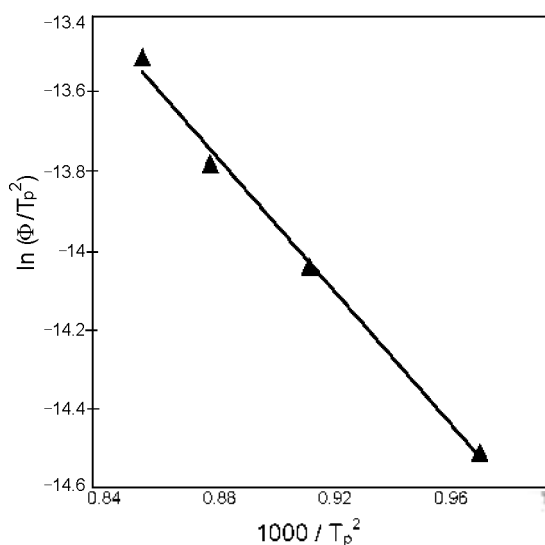
using the equations of Kissinger or Redhead as follows:<sup>24</sup>

$$\ln(\Phi/T_p^2) = -E/RT_p + \text{const.} \quad (4)$$

where  $\Phi$  is the heating rate,  $T_p$  is the peak temperature,  $R$  is the ideal gas constant. As shown in Figure 8, the plot of  $\ln(\Phi/T_p^2)$  vs.  $(1000/T_p)$  for the  $\text{Bi}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-TiO}_2$  containing precursor system showed a straight line. The energy required for the



**Figure 7.** The DTA patterns for the PC sample precursor in the temperature range of 200 - 600 °C for various heating rates of 10, 20, 30 and 40 K minute<sup>-1</sup>.



**Figure 8.** The plot of  $\ln(\Phi/T_p^2)$  vs.  $(1000/T_p^2)$  for the PC sample to obtain the activation energy involved in crystallization in the phase transformation from  $\text{Bi}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-TiO}_2$  containing precursor system to the Aurivillius phase  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ .

phase transformation from  $\text{Bi}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-TiO}_2$  containing precursor system to the Aurivillius phase  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  was found to be 69.8 kJ/mol as estimated from the slope of the straight line. This crystallization energy is one of the important factors to consider for the fabrication of the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  photocatalysts. This is because in case of SSR sample,  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase formed at 1030 °C, whereas in PC sample it was found crystallize at a temperature of at least 130 °C lower value. Therefore, with the knowledge of the activation energy one can always optimize the fabrication of high crystallinity/high specific surface as required for the visible light active photocatalyst.

## Conclusions

We have synthesized single phase  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  (BTFO) nanocrystals by simple polymerized complex method. The phase formation kinetics was studied by using structural and thermal analysis indicating that the crystallization of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  layered perovskite exhibiting Aurivillius phase was achieved in the temperature range of 800 to 1050 °C. The activation energy for grain growth of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  crystals in the  $\text{Bi}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-TiO}_2$  system formed by PC method was much lower than that for SSR method. That is, the pure  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase formation was found to occur at a relatively lower temperature by the PC method than by SSR method. Therefore, the study on the formation kinetics of BTFO has an important meaning in effective synthesis of nanocrystal materials as well as the development of highly efficient visible photocatalyst.

**Acknowledgments.** This work has been supported by KBSI grant T29320, MKE-RTI04-0201, KOSEF grant (NCRCP, R15-2006-022-01002-0), Hydrogen Energy R&D Center, Korea.

## References

- Kim, H. G.; Hwang, D. W.; Lee, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 8912.
- Maeda, K.; Takata, T.; Hara, M.; Saito, N.; Inoue, Y.; Kobayashi, H.; Domen, K. *J. Am. Chem. Soc.* **2005**, *127*, 8286.
- Kim, S. W.; Khan, R.; Kim, T. J.; Kim, W. *Bull. Korean Chem. Soc.* **2008**, *29*, 1217.
- Hitoki, G.; Takata, T.; Kondo, J.; Hara, M.; Kobayashi, H.; Domen, K. *Chem. Commun.* **2002**, 1698.
- Asahi, R.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science* **2001**, *293*, 269.
- Khan, S. M.; Al-Shahry, M.; Jr. Lugler, W. B. *Science* **2002**, *297*, 2243.
- Sakthivel, S.; Kisch, H. *Angew. Chem. Int. Ed.* **2003**, *42*, 4908.
- Subramanian, E.; Baeg, J.; Kale, B. B.; Lee, S. M.; Moon, S.; Kong, K. *Bull. Korean Chem. Soc.* **2007**, *28*, 2089.
- Jang, J. S.; Borse, P. H.; Lee, J. S.; Choi, S. H.; Kim, H. G. *J. Chem. Phys. C* **2008**, *128*, 154717.
- Jang, J. S.; Kim, H. G.; Borse, P. H.; Lee, J. S. *Inter. J. Hydrogen Energy* **2007**, *32*, 4786.
- Jang, J. S.; Kim, H. G.; Joshi, U. A.; Jang, J. W.; Lee, J. S. *Inter. J. Hydrogen Energy* **2008**, *33*, 5975.
- Kim, H. G.; Borse, P. H.; Choi, W.; Lee, J. S. *Angew. Chem. Int. Ed.* **2005**, *44*, 45859.
- Kim, H. G.; Jeong, E. D.; Borse, P. H.; Jeon, S.; Yong, K.; Lee, J. S.; Li, W.; Oh, S. H. *Appl. Phys. Lett.* **2006**, *89*, 064103.
- Jang, J. S.; Hwang, D. W.; Lee, J. S. *Catal. Today* **2007**, *120*, 174.
- Sun, S.; Wang, W.; Xu, H.; Zhou, L.; Shang, M.; Zhang, L. *J. Phys. Chem. C* **2008**, *112*, 17835.
- Kim, H. G.; Hwang, D. W.; Bae, S. W.; Jung, J. H.; Lee, J. S. *Catal. Lett.* **2003**, *91*, 193.
- Jung, E. D.; Borse, P. H.; Jang, J. S.; Lee, J. S.; Cho, C. R.; Bae, J. S.; Park, S.; Jung, O. S.; Ryu, S. M.; Kim, H. G. *J. Nanosci. Nanotech.* **2008**, *9*, 3568.
- Zhiqiang, Y.; Choi, K. M.; Jiang, N.; Park, S. E. *Bull. Korean Chem. Soc.* **2007**, *28*, 2029.
- Cullity, B. D. *Elements of X-ray Diffraction*, 2nd Edition; Addison-Wesley Publishing Company, Inc.: Reading, MA, 1978.
- Aurivillius, B. 1<sup>st</sup> Edition, *Ark. Kemi.* **1949**, *1*, 463.
- Subbaro, E. C. *Phys. Rev.* **1961**, *122*, 804.
- Coble, R. L. *J. Appl. Phys.* **1961**, *32*, 787.
- Jarcho, M.; Bolen, C. H.; Doremus, R. H. *J. Mater. Sci.* **1976**, *11*, 2027.
- Kissinger, H. E. *J. Res. Natl. Bur. Stand. (US)* **1956**, *57*, 217.