The Effect of Annealing on the Optoelectronic Properties and Energy State of Amorphous Pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$ Thin Layers by Sol–Gel Synthesis

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Abstract: Pyrochlore titanate ($\text{Y}_2\text{Ti}_2\text{O}_7$) is a promising material for a wide range of applications in optoelectronics and photocatalysis due to its advantageous chemical, mechanical, and optical properties. To enhance its potential for such uses, however, a high-quality and scalable synthesis method is required. We here investigate the crystallization of sol–gel produced $\text{Y}_2\text{Ti}_2\text{O}_7$ layers. We observe a transition of the amorphous pyrochlore phase at annealing temperatures below 700 °C. The transmittances of the $\text{Y}_2\text{Ti}_2\text{O}_7$ thin layers annealed at 400 to 700 °C are approximately 92.3%. The refractive indices and packing densities of $\text{Y}_2\text{Ti}_2\text{O}_7$ thin layers annealed at 400–700 °C/1 h vary from 1.931 to 1.954 and 0.835 to 0.846, respectively. The optical bandgap energies of $\text{Y}_2\text{Ti}_2\text{O}_7$ thin layers annealed at 400–700 °C/1 h reduce from 4.356 to 4.319 eV because of the Moss–Burstein effect. These good electronic and optical properties make $\text{Y}_2\text{Ti}_2\text{O}_7$ thin layers a promising host material for many potential applications.

Keywords: pyrochlore; $\text{Y}_2\text{Ti}_2\text{O}_7$; amorphous; sol–gel deposition; refractive index; bandgap energy; packing density

1. Introduction

Pyrochlore titanate ($\text{Y}_2\text{Ti}_2\text{O}_7$) is an important material because it has high mechanical [1,2], chemical [3], thermal stability [4,5], low phonon energy [4,6], good photocatalytic activity [7], a high refractive index [8], and excellent ion-electron conductivity [9,10], etc. Therefore, it has many applications, such as photocatalyst [11], solid-electrolytes of fuel cells [12,13], gas-sensing materials [14], high-K dielectrics [15,16], H$_2$ storage material [17], nuclear waste storage material [18], transistor device [19], and photovoltaic material [20]. Moreover, $\text{Y}_2\text{Ti}_2\text{O}_7$ can act as the host matrix of phosphor materials. The rare earth-doped $\text{Y}_2\text{Ti}_2\text{O}_7$ have attracted many researchers to pay attention to the application of fiber amplifiers [21], integrated electronic devices [22], up-conversion luminescence temperature sensing material [23–25], and visible up-conversion luminescent solar converter (LSC) in recent years [26].

To realize these applications, a large-scale synthesis approach is needed. To date, $\text{Y}_2\text{Ti}_2\text{O}_7$ nanocrystals or thin films have been produced by several approaches, such as coprecipitation [27,28], hydrothermal processes [29], mechanical milling [30,31], the liquid
mix technique [32], solid-state reaction [33,34], sol–gel processes [14,35,36], and aerosol-assisted chemical vapor deposition (AACVD) [20]. However, certain processes are not readily scalable due to stringent process conditions and complex preparation.

Sol–gel processes, on the other hand, have demonstrated the potential to produce large scale thin films using simple tools, such as printing and spin-coating. Such films are then annealed at high temperatures to enhance their performance.

We here systematically investigate the effects of annealing temperatures on the phase development, layer morphology, and related optoelectronic properties of $Y_2Ti_2O_7$ thin layers. We demonstrate that $Y_2Ti_2O_7$ thin layers have high average transmittance (73.8–75.1%), high refractive index (1.931–1.954 at $\lambda = 550$ nm), and high bandgap energy (4.319–4.356 eV), which depends on the variation of annealing temperatures (400–750 °C). Utilizing this understanding, we were able to produce high-quality $Y_2Ti_2O_7$ thin layers directly on a glass substrate. The good optoelectronic properties and scalable production open up new directions for $Y_2Ti_2O_7$-based applications.

2. Experimental Procedures

2.1. Fabrication of Sol–Gel Solution and Thin Layers

Titanium solution was prepared by mixing acetic acid (HAc, 99.9%, Merck, Darmstadt, Germany), titanium isoproxide ($\geq 99\%$, Acros, Geel, Belgium), and 2-methoxyethanol (2-MOE, 99.9%, Merck) in a molar ratio of Ti/HAc/2-MOE = 1/15/10. Yttrium solution was produced by mixing methanol (Me, $\geq 99.9\%$, Merck), ethylene glycol (EG, $\geq 99.9\%$, Alfa, Lancashire, UK), and yttrium acetate (Y(CH$_3$COO)$_3$·4H$_2$O, 99.9%, Alfa) with molar ratio of Y/Me/EG = 1/50/15 and dissolved into the titanium solution. Homogeneous hydrolysis reaction were completed by stirring the mixture solution for 10 h [37,38].

Subsequently, the $Y_2Ti_2O_7$ precursor solution was spin-coated on a Corning 7059 glass substrate at 1000 rpm for 10 s and then 3000 rpm for 30 s. Heating to 120 °C was conducted to dry the deposited sol–gel film. The dried sol–gel films were then pyrolyzed at 380 °C for 50 min in ambient atmosphere.

The sol–gel coating process and subsequent pyrolysis process was repeated eight times to obtain films of approximately 430 nm thickness. Afterwards, thin layers were annealed from 400 to 750 °C for 1 h in ambient conditions. The average layer thickness of $400 \pm 10$ nm and other property calculations (grain size, transmittance, refractive index, and optical bandgap) were obtained by averaging over five samples.

2.2. Characterization of Thin Layers

The $\alpha$-step profile meter (Alpha-Step IQ, KLA-Tencor, Milpitas, CA, USA) is utilized for the thickness of thin layers’ measurements. A scanning electron microscopy (SEM) (Hitachi, Tokyo, Japan, S4800-I) was performed at an accelerating voltage of 15 kV. A Shimadzu UV-2100 spectrophotometer was used for transmission spectra measurement of the $Y_2Ti_2O_7$ thin layer in the UV-visible range. X-ray diffraction (XRD) measurements of thin layers were performed by an X-ray diffractometer (Bruker, Billerica, MA, USA, D8 discovery) with CuK$\alpha$ radiation ($\lambda = 0.154$ nm).

3. Results and Discussion

3.1. Crystal Structure and Layer Morphology

The XRD patterns in Figure 1 show the effect of annealing at different temperatures (400, 500, 600, 700, and 750 °C) for 1 h on the phase transformation of $Y_2Ti_2O_7$ thin layers. For the annealing temperatures $\leq 700$ °C, $Y_2Ti_2O_7$ thin layers exhibit a weak broad continuum around $2\theta = \sim 30^\circ$ ((222) peak) which is the characteristic of an amorphous structure exhibiting short-range order. When the annealing temperature reaches 750 °C, the well-crystallized pyrochlore phase is identified by the (222), (311), (400), and (622) peaks (JCPDS No. 42-0413). No TiO$_2$, Y$_2$O$_3$, and other phases are observed in this system. This transition temperature between amorphous and crystalline $Y_2Ti_2O_7$ is in the range of previous reports on sol–gel processes, e.g., 725 [39], 750 [40], or 800 °C [35,36]. However,
the other sol–gel or AACVD methods can induce the formation of crystallized Y$_2$Ti$_2$O$_7$ phase at 550–570 °C [14,20]. The different starting materials and processes can result in the different crystalized temperatures and crystallinity.

The average grain size (D) of Y$_2$Ti$_2$O$_7$ thin layers is determined by the Scherrer equation [41]:

$$D = \frac{SA}{\sqrt{BM - BS \cos \theta}}$$  \hspace{1cm} (1)

where $S$ is the Scherrer constant (0.9), $\lambda$ is the wavelength of incident radiation, $\theta$ is the Bragg angle corresponding to the XRD peak being considered. $B_M$ and $B_S$ are the width in radians of one of the sample and standard (Si powder) diffraction peaks at half-maximum, respectively. The instrument broadening ($B_S$) is 0.14 in our system.

After calculation, the average estimated grain sizes of the Y$_2$Ti$_2$O$_7$ thin layers annealed at 600, 700, and 750 °C for 1 h are ~1.4 nm, ~1.5 nm, and ~32 nm, respectively. It is worth noting that the intensity of the broad (222) peak gradually increases when the annealing temperature increases from 400 to 700 °C. Furthermore, the crystals grow up and the XRD peak of the (222) facet becomes sharper at 750 °C. This means that the portion of amorphous Y$_2$Ti$_2$O$_7$ phase reduces as the crystallinity of Y$_2$Ti$_2$O$_7$ phase is enhanced. Due to the glass transition temperature of the Corning 7059 substrate, the annealing temperature range is limited to 750 °C.

![Figure 1. XRD patterns of the Y$_2$Ti$_2$O$_7$ thin layers annealed at the temperatures of 400 to 750 °C for 1 h. The 2θ positions for bulk Y$_2$Ti$_2$O$_7$ are shown on the plot for the reference.](image)

Figure 2 represents top-view SEM images of the Y$_2$Ti$_2$O$_7$ thin layers annealed at 400, 500, 600, 700, and 750 °C for 1 h. No crystal facets or signs of grain boundaries were detected when samples were annealed below 750 °C. This absence is expected from our XRD analysis, as the grain size of these films is below the resolution of the SEM. Conversely, crystal structures and grain boundaries can be observed at 750 °C annealing. As the surface of sol–gel spin coating thin films is very smooth, SEM images are not very clear.
3.2. Optoelectronic Properties

Figure 3 shows the effect of annealing temperatures on the transmittance spectra of the Y$_2$Ti$_2$O$_7$ thin layers annealed at 400, 500, 600, 700, and 750 °C for 1 h. The small fluctuation at high transmittances is due to the Fabry–Perot interference phenomenon of multiple reflected beams.

Figure 3. Transmittance spectra of the Y$_2$Ti$_2$O$_7$ thin layers annealed at the temperatures of 400 to 750 °C for 1 h.
For Y$_2$Ti$_2$O$_7$ thin layers annealed at 400, 500, 600, and 700 °C, the regular interference fringes indicate that all of the Y$_2$Ti$_2$O$_7$ thin layers have smooth interfaces and surfaces. The transmittance peaks of difference annealing temperatures slightly shift. Thin layers with different refractive indices result in the different optical path lengths for the constructive/destructive interference. However, Y$_2$Ti$_2$O$_7$ thin layers annealed at 750 °C exhibit more random interference. This effect originates from the surface melting of the glass substrate and other optical properties (transmittance, optical bandgap, and refractive index) of Y$_2$Ti$_2$O$_7$ thin layers annealed at 750 °C cannot be calculated.

The maximum transmittances in the wavelength ranging 200–1100 nm of the Y$_2$Ti$_2$O$_7$ thin layers annealed at 400–700 °C/1 h are approximately 92.3%. These amorphous thin layers have small grain size and low surface roughness resulting in the weak scattering and high transmittance.

The refractive index ($n$) of the Y$_2$Ti$_2$O$_7$ thin layer can be obtained from the transmittance spectra by fit to the Swanepoel and Cauchy equation [42]. Figure 4 shows the wavelength dependence of refractive indices for Y$_2$Ti$_2$O$_7$ thin layer annealed at 400, 500, 600, and 700 °C for 1 h. As the annealing temperature increases, the refractive index of the thin layer increases. The refractive indices are 1.931, 1.936, 1.941, and 1.954 at 500, 600, and 700 °C for 1 h, respectively. At higher temperatures, the crystallinity and densification of Y$_2$Ti$_2$O$_7$ thin layers are also improved, which leads the higher refractive indices of Y$_2$Ti$_2$O$_7$ thin layers. On the other hand, the refractive index of the amorphous phase is usually lower than that of high crystalline phase (e.g., the refractive index of bulk Y$_2$Ti$_2$O$_7$ is 2.34) [43].

![Figure 4](image_url)

**Figure 4.** Wavelength dependence of the refractive index for the Y$_2$Ti$_2$O$_7$ thin layers annealed at 400, 500, 600, and 700 °C for 1 h.

In addition, we calculate the degree of porosity in Y$_2$Ti$_2$O$_7$ thin layers. By following the Bragg–Pippard formula [44], the packing density ($p$) can be calculated using the following equation:

$$n_f^2 = \frac{(1 - P)n_v^4 + (1 + P)n_p^2 n_v^2}{(1 + P)n_v^2 + (1 - P)n_p^2}$$  \hspace{1cm} (2)

where $n_v$, $n_p$, and $n_f$ are the refractive indices of voids ($n_v = 1$ for empty voids), bulk materials, and porous layers, respectively. The packing densities of the Y$_2$Ti$_2$O$_7$ thin layers annealed at 400, 500, 600, and 700 °C for 1 h are 0.835, 0.837, 0.84, and 0.846, respectively. The packing density increases with annealing temperature, which is attributed to the significant increase in the crystallinity and reduction in the porosity.
Figure 5 plots the relationship of \((\alpha h \nu)^2\) versus photon energy \((E)\) of the \(\text{Y}_2\text{Ti}_2\text{O}_7\) thin layers annealed at 400–700 °C/1 h, and the extrapolated optical bandgap energies of thin layers were determined.

**Figure 5.** (a) \((\alpha h \nu)^2\) as a function of photon energy \((E)\) of the \(\text{Y}_2\text{Ti}_2\text{O}_7\) thin layers annealed at 400–700 °C/1 h. (b) Enlarged diagram of (a). (c) Optical bandgap as a function of annealing temperatures. The error bars represent the statistical deviation among five samples.

The optical bandgap energy \((E_g)\) of thin layer can be related to absorption coefficient \((\alpha)\) by Equation (3)

\[
\alpha h \nu = \text{const.} \,(h \nu - E_g)^m
\]

Equation (3)
where $m = 1/2, 3/2, 2$ or $3$ indicates allowed direct, forbidden direct, allowed indirect, and forbidden indirect electronic transitions, respectively [45]. A better linear dependence can be found in the $(\alpha h\nu)^{1/m}$ versus $E$ plots at $m = 1/2$ for all thin layers, which means the $Y_2Ti_2O_7$ thin layer belongs to direct-transition-type material.

As shown in Figure 5, the optical bandgap energy decrements from 4.356 to 4.319 eV were observed when the $Y_2Ti_2O_7$ thin layers annealing temperatures increase from 400 to 700 °C. These optical bandgap energies are higher than that of the crystallized $Y_2Ti_2O_7$ thin films [14]. There are several causes or aspects, such as grain size [46,47], thickness [46,48], stress [49], and defects [50,51] could affect or shift the bandgap energy of thin layer materials. For the amorphous $Y_2Ti_2O_7$ thin layers annealed from 400 to 700 °C, however, this red shift of bandgap energy could be mainly attributed to defects.

Many defects such as unsaturated bonds, dangling bonds, interstitial atoms, and vacancies can exist in amorphous structure. In general, oxygen vacancies can be observed in many transition metal oxide thin layers such as ZnO [52], Ba$_x$Sr$_{1-x}$TiO$_3$ [53,54], CdIn$_2$O$_4$ [55,56], WO$_3$ [57,58], and TiO$_2$ [59]. Moreover, enormous oxygen vacancies can exist in the $Y_2Ti_2O_7$ lattice because the large unit cell of $Y_2Ti_2O_7$ allows some of the oxygen ions to move relatively freely, which results in the formation of small polarons [57]. Therefore, oxygen vacancies could be the dominant vacancy defects in amorphous $Y_2Ti_2O_7$ thin layers.

According to the defect reaction equation, two free charge carriers can be generated from the creation of one oxygen vacancy [60]. Like the Moss–Burstein effect, the lowest state of the conduction band is blocked by these free charge carriers, resulting in an increase in the optical bandgap energy [61,62]. After higher temperature annealing, the crystallization of amorphous $Y_2Ti_2O_7$ thin layers was improved with the annihilation of oxygen vacancies, which is associated with the reduction in free charge carriers and the decrease in the optical bandgap energy, as shown in Figure 6.

![Schematic representation of the Burstein–Moss (B-M) shift for the $Y_2Ti_2O_7$ thin layers annealed at 400 and 700 °C for 1 h.](image)

**Figure 6.** Schematic representation of the Burstein–Moss (B-M) shift for the $Y_2Ti_2O_7$ thin layers annealed at 400 and 700 °C for 1 h.

### 4. Conclusions

$Y_2Ti_2O_7$ thin layers with a thickness of ~400 nm thin layers were fabricated by the sol–gel technique. At annealing temperatures below 700 °C, all thin layers maintain an amorphous structure. The maximum transmittance of amorphous thin layers is approximately 92.3%. The transmittance is high because of small grain size, low surface roughness, and weak scattering. The refractive indices and optical bandgap energies of $Y_2Ti_2O_7$ thin layers are strongly related to the annealing temperatures. The enlarged refractive indices with the increase in annealing temperatures are attributed to thin layers with the improved densification and crystallinity. The refractive indices ($n$ at $\lambda = 550$ nm) of $Y_2Ti_2O_7$ thin layers can be altered from 1.931 to 1.954 as the annealing temperature raises from 400 to 700 °C/1 h.
The amorphous $\text{Y}_2\text{Ti}_2\text{O}_7$ thin layers annealed at higher temperatures possess smaller optical bandgap energy (4.319 eV), which could be attributed to the Burstein–Moss shift.


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