Progress in Ti$_3$O$_5$: Synthesis, properties and applications

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Abstract: The crystal structure, physical, chemical and phase transition properties of trititanium pentoxide (Ti$_3$O$_5$) have aroused a broad range of research effort since the 1950s. Different crystalline forms ($\alpha$, $\beta$, $\gamma$, $\delta$, and $\lambda$) of Ti$_3$O$_5$ exhibit various properties. Particularly, reversible phase transitions between $\lambda$- and $\beta$-Ti$_3$O$_5$ have been attracting increasing research interest, which brings new potential applications of Ti$_3$O$_5$ materials in the field of energy and data storage. More recently, Ti$_3$O$_5$ materials have shown excellent performance in trace detection, microwave absorption and virus adsorption, which has expanded its application fields. Here, the essential properties of different crystal forms of Ti$_3$O$_5$ are described in detail. An intensive overview of Ti$_3$O$_5$ preparation methods and applications is comprehensively summarized.

Key words: Ti$_3$O$_5$; phase transition; pressure induction; data storage; catalyst support

1 Introduction

Aside from stoichiometric titanium dioxide (TiO$_2$), which has been studied extensively and used in numerous fields ranging from alloys to photo-catalytic materials, titanium binary oxides have a series of suboxides. These titanium suboxides comply with the generic formula of Ti$_n$O$_{2n-1}$ and include NaCl-type TiO, corundum-type Ti$_2$O$_3$ and “Magnéli phases” Ti$_n$O$_{2n-1}$ ($n\geq 3$) [1−12]. However, whether trititanium pentoxide (Ti$_3$O$_5$) belongs to this series remains controversial because the typical shear planes existing in Magnéli phases are not found in the crystal structure [13−15].

Since the 1950s, many scholars have conducted considerable research on Ti$_3$O$_5$. Yet, the focus is mostly on structure, physical and chemical properties, and five different Ti$_3$O$_5$ crystal structures ($\alpha$, $\beta$, $\gamma$, $\delta$, and $\lambda$) have been identified [16]. These phases are closely related structurally and exhibit different properties in terms of conductivity, magnetism and electronic structure. In addition, there are some intriguing phase-transition characteristics between them under different external conditions. At room temperature, bulk Ti$_3$O$_5$ is kept in the form of a stable $\beta$ phase with a monoclinic structure. However, this phase transforms into the $\lambda$ phase at 460 K with an isostuctural phase transition and further transforms into the $\alpha$ phase at 514 K, undergoing a structural...
transition from monoclinic to orthorhombic. $\gamma$-Ti$_3$O$_5$ can be obtained through slow cooling of $\alpha$-Ti$_3$O$_5$ at high temperatures, transforming into $\delta$-Ti$_3$O$_5$ at approximately 237 K.

Recently, the research on Ti$_3$O$_5$ has mainly focused on its preparation methods and applications as functional materials, as shown in Fig. 1. In 2003, the first applications of Ti$_3$O$_5$ for oxygen sensors were reported. The features of metal-like and variable atom ratio of oxygen to titanium confer $\alpha$-Ti$_3$O$_5$ potential applications in oxygen sensors. TiO$_2$ is a widely studied photo-catalytic material, and titanium suboxides, such as Ti$_2$O$_3$, Ti$_4$O$_7$ and Ti$_8$O$_{15}$, also exhibit good photo-activity due to the existence of oxygen vacancies. Therefore, the photo-catalytic activity and performance of Ti$_3$O$_5$ have also been studied. Furthermore, Ti$_3$O$_5$ holds the advantages of good chemical stability, non-toxicity and good acid and alkali resistance through which it can be recommended for catalyst support applications. In addition, the discovery of the photo-induced phase transition between $\lambda$ and $\beta$ phases has raised a new discussion and piqued research interest in science, introducing new applications into optical memory. This intriguing reversible phase transition could also be triggered by other external stimulation, such as pressure, temperature and current, which further broadened the application of Ti$_3$O$_5$ in energy storage, THz sensors and smart windows [17]. Recently, the excellent performance of Ti$_3$O$_5$ in trace detection, microwave absorption and virus adsorption has provided broad prospects for its future application.

Although there are intensive experimental and computational studies, a comprehensive summary of the structure, physical properties, preparation and application of Ti$_3$O$_5$ is lacking. A deep understanding of the basic physicochemical properties of Ti$_3$O$_5$ might aid in developing applications in new areas. As a result, we initially discussed synthetic approaches of Ti$_3$O$_5$. Especially, we systematically discussed crystal and chemical structure properties of different crystal forms of Ti$_3$O$_5$, including reversible phase transition phenomena between them. Through this discussion, we summarized a comprehensive overview of the application of Ti$_3$O$_5$ in gas sensors, energy storage, optical storage media, catalysts and other new application fields. Finally, the focus for the future direction of Ti$_3$O$_5$ was provided.

2 Synthetic approaches for trititanium pentoxide (Ti$_3$O$_5$)

Numerous methods have been reported for preparing Ti$_3$O$_5$ since it was identified. Typically,
TiO$_2$ is selected as the raw material for preparing Ti$_3$O$_5$ by using reduction methods, and metal titanium, carbon, carbonaceous organic material or reducing atmosphere (H$_2$, CO) can be used as reducing agents for preparing Ti$_3$O$_5$ using reduction methods. Reducing agents, which have a higher oxygen affinity, are oxidized to their corresponding oxides, reducing TiO$_2$ to Ti$_3$O$_5$, simultaneously. In addition, some methods such as electro-chemical reduction and pulsed laser deposition (PLD) are also used to meet the need to obtain different forms or properties of Ti$_3$O$_5$.

2.1 Metallothermic reduction

Metal titanium is the most commonly used reductant at the start of the preparation of Ti$_3$O$_5$. The key to preparing a high purity target product lies in the appropriate ratio of titanium to TiO$_2$. The reduction processes work at temperatures above 1000 °C under an inert atmosphere for several days using an electric arc furnace or electric resistance furnace, as shown in Fig. 2. The redox reaction is given as follows:

$$\text{Ti}(s)+5\text{TiO}_2(s)=2\text{Ti}_3\text{O}_5(s)$$  \hspace{1cm} (1)

For instance, in the experiments of ÅSBRINK and MAGNÉLI [18], TiO$_2$ and Ti were used as raw materials and mixed with a stoichiometric ratio to prepare Ti$_3$O$_5$ using an electric arc furnace under an argon atmosphere. After two-week annealing at 1150 °C, high-quality $\beta$-Ti$_3$O$_5$ was obtained. To prepare $\gamma$-Ti$_3$O$_5$ films, KUROKAWA et al [19] firstly synthesized Ti$_2$O$_3$ by sintering mixed Ti and TiO$_2$ pellets at 1000 °C for 12 h. Secondly, $\gamma$-Ti$_3$O$_5$ films grew on $\alpha$-Al$_2$O$_3$ (0001) substrates using Ti$_2$O$_3$ as a target by the PLD method. Using the same method, FAN et al [20] used titanium metal as a target to directly grow $\gamma$-Ti$_3$O$_5$ on $\alpha$-Al$_2$O$_3$ (0001) substrates by tuning the oxygen pressure. In contrast to other reported targets, titanium has the advantage of easily preparing Ti$_3$O$_5$ films because this is an exothermic process and the oxygen content is easy to control. Titanium is an ideal reductant because no impurities are introduced in this process. However, this method is limited by high costs and prolonged treatment time.

In addition, KITADA et al [21] selected Zr as a reductant and TiO$_2$ as a titanium source using the sol–gel method to prepare macroporous titanium suboxides (Ti$_n$O$_{2n-1}$; $n=2, 3, 4, 6$). Firstly, porous TiO$_2$ precursor monolith was fabricated using ethyl acetoacetate as a chelating agent and NH$_4$NO$_3$ as mineral salt. Then, several suboxides were obtained under different reduction degrees depending on the amount of the reductant. A single phase of Ti$_3$O$_5$ can be prepared under a 6:1.05 molar ratio of TiO$_2$ to Zr at 1150 °C. The as-prepared Ti$_3$O$_5$ had a macroporous structure with low bulk densities (1.78 g/cm$^3$) and large porosities (58%).

2.2 Carbothermal reduction

To develop an efficient, economical and rapid method for preparing nano-$\lambda$-Ti$_3$O$_5$, CHAI et al [22] proposed a carbothermal reduction method. The redox reaction is given as follows:

$$3\text{TiO}_2(s)+\text{C}(s)=\text{Ti}_3\text{O}_5(s)+\text{CO}(g)$$  \hspace{1cm} (2)

The key to preparing a high purity target product lies in the appropriate ratio of carbon to TiO$_2$. In addition, the roasting temperature, holding time and argon gas flow rate were also studied in detail. $\lambda$-Ti$_3$O$_5$ was synthesized at 1050 °C under 4.5 wt.% carbon black content for 3 h in an inert atmosphere. The resulting powder had a specific surface area of 12.82 m$^2$/g with an average particle size of (3.0±1.0) µm. After that, using the same reduction approach, they reported the effect of coating layers, such as Al$_2$O$_3$ or SiO$_2$, on the formation of nano-$\lambda$-Ti$_3$O$_5$. In 2020, a new approach using commercial polyethylene glycol 600 as a carbon source and tetra-$n$-butyl titanate as a titanium source was reported by CAI et al [23]. Spherical shape powder with an average particle size of 40 nm was obtained at 1070 °C for 2 h. Subsequently, YANG et al [24] were inspired by the preparation of Ti$_n$O$_{2n-1}$ using polyvinyl alcohol as a carbon source and proposed using phenol resin, which had highly reduced properties, as reducing agents to prepare recorded purity $\beta$-Ti$_3$O$_5$ compacts. The $\beta$-Ti$_3$O$_5$ of the final product was as high as 98.06% according to X-ray diffraction (XRD) refinement results.

The carbothermal reduction has unique...
advantages such as high yield and economic and environmental friendliness; however, it is difficult to avoid carbon residue within the as-prepared Ti$_3$O$_5$.

### 2.3 Hydrogen reduction

In 1968, IWASAKI et al [25] used TiO$_2$ as a titanium source and H$_2$ as a reductant to synthesize Ti$_3$O$_5$. A D-type phase, hereafter called $\lambda$-Ti$_3$O$_5$, was obtained at 1250 °C for 3 h in a hydrogen gas stream. The redox reaction is given as follows:

$$3\text{TiO}_2(s) + \text{H}_2(g) \rightarrow \text{Ti}_3\text{O}_5(s) + \text{H}_2\text{O} (g)$$  (3)

To prepare $\alpha$-Ti$_3$O$_5$ thin films, ZHENG [26] used Ti(OC$_4$H$_9$)$_4$ as a titanium resource to obtain Ti$^{4+}$ containing sol. Firstly, TiO$_2$ thin films were fabricated by a dip-coating method on Al$_2$O$_3$ substrates. Secondly, after reducing these TiO$_2$ thin films with hydrogen at 1200 °C for 4 h, $\alpha$-Ti$_3$O$_5$ thin films were formed. To prepare nano-$\lambda$-Ti$_3$O$_5$, OHKOSHI et al [27] selected TiO$_2$ as raw material and reduced it under hydrogen stream (0.3 dm$^3$/min) at 1200 °C for 2 h. The prepared crystals were composed of nano-crystals in (25±15) nm with a flake form. In addition, a combination of reverse-micelle and sol–gel method was also used to synthesize nano-$\lambda$-Ti$_3$O$_5$. The process is illustrated in Fig. 3 [28], and the prepared sample has a cubic shape with (21±11) nm. Using this approach, NASU et al [28] synthesized different grain sizes of $\lambda$-Ti$_3$O$_5$ by controlling the sintering temperature; however, the hydrogen flow rate did not influence it.

In the experiments of ALIPOUR MOGHADAM ESFAHANI et al [29], to obtain catalyst support that contains Ti$_3$O$_5$, TiO$_2$ was selected as a titanium source and a gaseous mixture containing hydrogen (H$_2$:N$_2$10:90, vol.%) as a reducing agent. The problems of carbon residue and other impurities can be solved well; however, the potential explosion hazard restricts its applications.

### 2.4 Carbon monoxide reduction

In addition to hydrogen reduction, crystal growth under CO reducing atmosphere is also a practical method for preparing Ti$_3$O$_5$ in the early years. For instance, BARTHOLOMEW and WHITE [30] successfully grew Ti$_3$O$_5$ from Na$_2$B$_2$O$_3$–B$_2$O$_3$ flux by controlling oxygen fugacity under the CO atmosphere, which originated from graphite. The Ti$_3$O$_5$ single crystal was obtained under a certain oxygen fugacity at 1300 °C.

### 2.5 Electro-chemical reduction

Since the electro-chemical de-oxidization of TiO$_2$ in molten calcium chloride to directly prepare titanium was proposed by CHEN et al [31] many scholars have dedicated effort to the in-depth study of this process [31,32]. DRING et al [33] investigated cathodic de-oxygenation of TiO$_2$ at 900 °C under certain potentials lower than those of the formation of calcium. The reduction from TiO$_2$ to Ti$_3$O$_5$ was detected at a potential of 300 mV, which was negative for the TiO$_2$ open-circuit on the TiO$_2$ working electrode. Further studies on pre-dominance diagrams were also conducted by them to better understand the electro-chemical de-oxidization of TiO$_2$ [34]. On this basis, the kinetic parameters related to different reduction processes were calculated by KAR and EVANS [35] using a coupled electro-chemical and diffusion model. These studies have demonstrated the feasibility and availability of the proposed approach; however, they mainly focused on electro-chemical de-oxidization processes of TiO$_2$ rather than the preparation of Ti$_3$O$_5$. After that, ERTEKIN et al [36] developed a one-step electro-deposition method for synthesizing Ti$_3$O$_5$ films by an electro-deposition method using an acetonitrile solution as a supporting electrolyte. TiOSO$_4$ and H$_2$O$_2$ play a major role in this process, and both $\gamma$-Ti$_3$O$_5$ and $\lambda$-Ti$_3$O$_5$ can be obtained from indium–tin–oxide coated glass substrates at certain potentials and

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**Fig. 3** Schematic of $\lambda$-Ti$_3$O$_5$ nano-crystal synthesis process [28]. Reproduced with permission. Copyright 2014, Institute of Physics Publishing
temperatures. In their follow-up work, $\beta$-Ti$_3$O$_5$ was also detected on the substrates using the same methods [37]. These studies provided a new idea for preparing Ti$_3$O$_5$ thin films with the advantage of without requiring additional heating. However, the obtained products are a complex mixture of titanium sub-oxides or a mixture of Ti$_3$O$_5$ with different crystals. Therefore, further optimization regarding deposition conditions is needed.

2.6 Chemical vapor transport
In addition, a cheaper, efficient and easy method called chemical vapour transport was applied to the crystal growth of Ti$_3$O$_5$ [38]. After that, a series of titanium suboxide crystals were fabricated using this method. MERCIER et al [39] selected TiO$_2$ as the starting material and used hydrogen to reduce it to the desired suboxide. Then, they selected TeCl$_4$ or NH$_4$Cl as a transport agent for the single-phase growth of Ti$_3$O$_5$. STROBEL and PAGE [40] used TeCl$_4$ or Cl$_2$ as a transport agent to prepare Ti$_2$O$_{2n-1}$ with $n=2$–9. Most of the samples were twinned crystals because of the particular sensitivity of Ti$_3$O$_5$ to oxygen. In experiments of HONG [41], commercial TiO$_2$ and titanium were used as raw materials, and they were mixed at a suitable stoichiometric ratio. The mixed powders were annealed in an arc furnace under an argon atmosphere to obtain Ti$_2$O$_3$ and $\beta$-Ti$_3$O$_5$, which were mixed in stoichiometric proportions. Then, the obtained mixtures were pressed into pellets, which were used to prepare single crystals of $\gamma$-Ti$_3$O$_5$ using TiCl$_4$ as a transport agent. Notably, this is the first report on the preparation of single crystals of $\gamma$-Ti$_3$O$_5$. After that, the crystal structure and physical properties of $\gamma$-Ti$_3$O$_5$ were studied systematically by HONG and ÅSBRINK [42].

3 Structures and properties

3.1 Phase structures
Ti$_3$O$_5$ is a polycrystalline compound with variable crystallographic structures ($\beta$, $\lambda$, $\alpha$, $\gamma$, and $\delta$). The schematic representation and lattice parameters of the different crystal structures are shown in Fig. 4 and Table 1 ($\beta$ phase: ICSD card No. 75194; $\lambda$ phase: ICSD card No. 75193; $\alpha$ phase: ICSD card No. 50984; $\gamma$ phase: ICSD card No. 35148; $\delta$ phase: CCDC card No. 1004604).

$\beta$-Ti$_3$O$_5$, originally known as the LM (low-temperature) structure, is a stable phase at room temperature with a monoclinic symmetry and space group $C2/m$. Figure 4(a) shows that there are three independent Ti atomic sites, labelled Ti(1), Ti(2) and Ti(3), respectively and each of them is octahedrally coordinated to six oxygen atoms, forming a distorted TiO$_6$ structure. The crystal could be viewed as comprising TiO$_6$ by sharing corners on the $b$-axis and edges in the $ac$ plane. The average valences for Ti(1), Ti(2) and Ti(3) are 3.0, 3.7 and 3.3, respectively [43]. $\lambda$-Ti$_3$O$_5$, originally known as the HM (high-temperature) structure, is a meta-stable phase with monoclinic symmetry and space group $C2/m$. As shown in Fig. 4(b), distorted TiO$_6$ shares six edges with its neighbours. This specialised junction makes Ti atoms with the same atomic environment, and the average valence is 3.3. $\alpha$-Ti$_3$O$_5$, hereafter called the HO (high temperature orthorhombic) structure, with orthorhombic symmetry and space group $Cmcm$ is a high-temperature phase [44]. Figure 4(c) shows that the crystal could be viewed as comprising TiO$_6$ by sharing corners on an axis and sharing six edges with its neighbours. There are two independent Ti atomic sites, labelled Ti(1) and Ti(2), respectively and their average valence is 3.3. $\gamma$-Ti$_3$O$_5$, which is another stable phase at room temperature with monoclinic symmetry and space group $I2/c$. It was reported by ÄSBRINK et al [45], and the structure is shown in Fig. 4(d). There are two independent Ti atomic sites, labelled Ti(1) and Ti(2), respectively and the crystal structure could be viewed as comprising two characteristic chains. One chain is made of regular Ti(1)O$_6$ octahedra joined by shared corners, whereas the other one has distorted Ti(2)O$_6$ octahedra joined by shared edges and a common face. The valence states for Ti(1) and Ti(2) are 3.36 and 3.30, respectively. In $\delta$-Ti$_3$O$_5$ (Fig. 4(e)), the Ti(1) site of $\gamma$-Ti$_3$O$_5$ becomes two different sites, labelling Ti(1a) and Ti(1b), respectively, thereby forming three independent Ti atomic sites, with corresponding valence states of 3.66, 3.16 and 3.2, respectively [46].

3.2 Phase transition properties
Phase transitions between Ti$_3$O$_5$ phases have been identified in numerous studies. These phases experience different transition processes during
Fig. 4 Schematics of crystal structures of Ti$_3$O$_5$ (β, λ, α, γ and δ)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal system</th>
<th>Space group</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>β/(°)</th>
<th>V/Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Ti$_3$O$_5$</td>
<td>Monoclinic</td>
<td>C2/m</td>
<td>9.7568 (2)</td>
<td>3.80077 (9)</td>
<td>9.4389 (1)</td>
<td>91.547 (1)</td>
<td>349.9</td>
</tr>
<tr>
<td>λ-Ti$_3$O$_5$</td>
<td>Monoclinic</td>
<td>C2/m</td>
<td>9.8261 (2)</td>
<td>3.78937 (9)</td>
<td>9.9694 (2)</td>
<td>91.258 (2)</td>
<td>371.12</td>
</tr>
<tr>
<td>α-Ti$_3$O$_5$</td>
<td>Orthorhombic</td>
<td>Cmcm</td>
<td>3.798 (2)</td>
<td>9.846 (3)</td>
<td>9.988 (4)</td>
<td>90</td>
<td>373.5</td>
</tr>
<tr>
<td>γ-Ti$_3$O$_5$</td>
<td>Monoclinic</td>
<td>P2/c</td>
<td>9.9701 (5)</td>
<td>5.0747(3)</td>
<td>7.1810(4)</td>
<td>109.865(4)</td>
<td>341.71</td>
</tr>
<tr>
<td>δ-Ti$_3$O$_5$</td>
<td>Monoclinic</td>
<td>P2/a</td>
<td>9.9651(7)</td>
<td>5.0604(4)</td>
<td>7.2114(5)</td>
<td>109.3324(9)</td>
<td>343.15(4)</td>
</tr>
</tbody>
</table>

warming and cooling with corresponding changes in lattice parameters, magnetic state and electric resistivity. During the heating process, the room-temperature stable β phase transforms into a meta-stable λ phase at approximately 460 K with the first-order phase transition and an abrupt
reduction of resistivity from semiconductors to metals [47,48]. The lattice parameters are also changed, especially the expansion of the c-axis, increasing the volume. As the temperature is increased to 514 K, the λ phase further transforms into the α phase with the second-order phase transition [49]. However, there is no sudden change in the magnetic state and resistivity. The meta-stable λ phases can be stabilized at room temperature by introducing impurity elements such as Fe, V, Mg, Li and Al, and with an increase in impurity content, the transition temperature is decreased accordingly [50−55]. In addition, the meta-stable λ phase could also be stabilized at room temperature in nano-scale, exhibiting a reversible phase transition between λ and β by an external stimulus such as laser light, pressure, temperature and current [56].

During the cooling process, the room-temperature stable γ phase transforms into the δ phase at approximately 237 K, which undergoes a Mott–Hubbard metal-insulator phase transition due to the breaking of a one-dimensionally conducting pathway, as shown in Fig. 5 [46]. From the electrical conductivity and optical measurement results, the γ phase has metallic conductor properties, whereas the δ phase exhibits semiconductor properties, as shown in Fig. 5(b). However, different results were obtained in terms of phase-transition temperature (225 K) in the thin film of the γ phase [57]. The most likely reason would be internal stress or strain caused by lattice-constant mismatches and different expansion coefficients between the substrate and product.

4 Applications of trititanium pentoxide (Ti₃O₅)

4.1 Gas sensor

Ti₃O₅ is considered the most promising gas sensor substitute in high-temperature solid-state gas sensors. ZHENG [58] used α-Ti₃O₅ in oxygen sensing for the first time. α-Ti₃O₅ thin films were synthesized by hydrogen reduction TiO₂ thin films, which were obtained on Al₂O₃ substrates using Ti(OC₄H₉)₄ as a precursor. The α-Ti₃O₅ thin films exhibited an impressive low resistivity−temperature coefficient with better high-temperature stability and reproducibility. However, their oxygen sensitivity needs to be further improved. After that, significant improvements in oxygen sensitivity and response rate were achieved by 5 at.% Ce and 1 at.% W doping, which offer more effective active sites on the surface of materials [26]. Compared with pure α-Ti₃O₅, W doping reduced the resistivity−temperature coefficient, whereas Ce doping increased the structure stable temperature to 700 °C. ZHANG et al [59] synthesized Ti₃O₅ sub-micron
rods by a sintering method using H2TiO3 nano-fibers as a precursor. However, the sensor characteristics are not satisfactory.

LI et al [60] prepared β-Ti3O5 by carbothermal reduction of TiO2, demonstrating certain oxygen sensitivity by experiment and density functional theory (DFT) calculations. However, its performance is not good based on the response and recovery time in 20% O2+80% N2 and 20% H2+80% N2 atmospheres. Therefore, further optimization is required.

4.2 Energy storage material

λ-Ti3O5 is a meta-stable phase and frequently appears at high temperatures. OHKOSHI et al [27,56] found that λ-Ti3O5 could exist at room temperature with nano-scale ((25±15) nm or (21±11) nm) due to thermodynamic local energy minimum. The as-prepared nano-λ-Ti3O5 was a metallic conductor and showed Pauli paramagnet. In addition, they found a reversible phase transition phenomenon between λ and β phases. It can be induced by laser light, which confers enormous potential in optical storage media. Subsequently, TOKORO et al [61] reported other induced reversible phase-transition factors, such as pressure, temperature and current, and specifically, λ-Ti3O5 could transform into β-Ti3O5 under external pressure with heat release. Vice versa, β-Ti3O5 could absorb heat from the external environment, transforming it into λ-Ti3O5 under external stimuli such as heat, current and light. This feature gives Ti3O5 enormous potential in heat storage. The absorbed energy during the phase transition from β to λ was (230±20) kJ/L with an induced temperature, and (240±40) kJ/L energy was released from λ to β with an induced pressure.

Because λ-Ti3O5 can only exist at room temperature with nano-scale, WEI et al [62] studied the effect of coating layers on the stability of meta-stable phase λ-Ti3O5. In their experiment, inorganic layers, such as Al2O3 or SiO2, were coated on the nano-rutile TiO2 particles to prepare λ-Ti3O5. Results indicated that the Al2O3−SiO2 dual-coated TiO2 sample emerged as λ-Ti3O5. However, a similar phenomenon was not found in the uncoated or SiO2-coated TiO2 sample. Therefore, the introduction of Al3+ from the coating layer played an important role in the formation and stabilization of λ-Ti3O5. After that, they proposed a doping strategy to investigate the stabilizing effect of Al3+ on λ-Ti3O5 [63]. From the d-spacing of the (110) plane, the value of the Al3+ doped sample (0.35 nm) was lower than the typical value (0.37 nm), indicating that Al3+ was doped in the substitutional mode. The as-prepared samples could exist at room temperature with a micro-crystal scale (2 µm) under 6.0 at.% Al doping. Furthermore, the effect of Al3+ doping on phase transition was extensively investigated. The results indicated that Al3+ doping not only reduced the transition temperature (β→λ) but also promoted the transition from β to λ. In 2019, WANG et al [64], inspired by the reference to the MgO−TiO2 equilibrium phase diagram, proposed an Mg doping strategy to stabilize λ-Ti3O5 at room temperature. Similar results concerning phase-transition properties were obtained. Note that the stabilization effects of Mg doping were more efficient than those of Al doping in terms of requiring less amount of Al3+. A possible reason was the larger ionic radius and lower valence of Mg2+.

In 2019, OHKOSHI et al [65] prepared a heat storage ceramic and used it to recycle waste heat from automobiles. The grain size of as-prepared λ-Ti3O5 was 10 times larger than that of previous samples of hydrogen reduction, called block-type λ-Ti3O5. From pressure-induced results, the phase transition from λ to β required a relatively low external pressure (50% transforms under 7 MPa). Temperature-induced results showed that the endothermic peak was at approximately 471 K (198 °C) with 237 kJ/L. After that, inspired by the aforementioned metal doping strategy, NAKAMURA et al [66] calculated the formation energy of λ-Ti3O5 with 54 different doping elements, and the results indicated that only six elements (Sc, Zr, Nb, Hf, Ta and W) promoted the formation of the λ phase with lower formation energy. Subsequently, bulk Ti3O5 was prepared using TiO2 as a titanium source and Ti as a reductant with different doping elements by an arc-melting technique, as shown in Fig. 6 [66]. However, only Sc doping formed the λ phase according to the XRD result. Sc doping content materials were synthesized, and the chemical formulas were Sc0.09Ti2.91O5, Sc0.105Ti2.895O5 and Sc0.108Ti2.92O5. Temperature-induced results showed that the corresponding endothermic peaks were at about 67, 45 and 38 °C, respectively. Compared with
Fig. 6 (a) Schematic of synthetic process of bulk $\lambda$-Sc$_{0.09}$Ti$_{2.91}$O$_5$; (b) Synchrotron X-ray diffraction patterns of pressure and temperature-induced phase-transition process; (c) Phase fractions at different pressures; (d) Endothermic performance from $\beta$ to $\lambda$ [66]. Reproduced with permission. Copyright 2020, Science

Previously reported storage ceramics, the capacity of energy storage (75 kJ/L) has been decreased by more than two-thirds. However, the critical transition temperature from $\beta$ to $\lambda$ decreased substantially, thereby providing a wider range of applications, as shown in Fig. 6(d). It shows great potential for use in power plants through the absorption of thermal energy from hot water. However, the relatively high pressure of the transformation from $\lambda$ to $\beta$ will be a challenge in practical applications.

SUN et al [67] reported Ti$_3$O$_5$ nano-film combined with carbon nano-tubes (CNTs)/Ni obtained by the PLD method under vacuum and
showed improved performance as super-capacitors due to the core–shell nano-structure of Ti$_3$O$_5$@CNTs/Ni, as shown in Fig. 7. In contrast to those regular TiO$_2$-based super-capacitors, Ti$_3$O$_5$@CNTs/Ni showed an excellent specific capacitance of 445.7 F/g at a rate capacity of 1 A/g. The DFT calculation results indicated that the formation of Ti$_3$O$_5$ led to a substantial reduction in the band gap compared with TiO$_2$.

The above observations strongly confirm that Ti$_3$O$_5$ holds promise for energy storage applications.

### 4.3 Optical storage media

In 2010, OHKOSHI et al. [27] synthesized nano-crystalline $\lambda$-Ti$_3$O$_5$ and showed photo-induced reversible properties between $\lambda$ and $\beta$ phases, as shown in Fig. 8. It was the firstly reported that Ti$_3$O$_5$ possessed photo-induced phase transition at room temperature. $\lambda$-Ti$_3$O$_5$ showed...
light absorption across a broad range of wavelengths, so the reversible phenomenon was observed under different incident nano-second-pulsed laser light (355, 532 and 1064 nm), which conferred Ti$_3$O$_5$ enormous potential in optical storage media. In addition, $\lambda$-Ti$_3$O$_5$ could also be obtained with continuous-wave laser irradiation from $\beta$-Ti$_3$O$_5$ to $\alpha$-Ti$_3$O$_5$ to $\lambda$-Ti$_3$O$_5$, as shown in Fig. 8(d). These features make Ti$_3$O$_5$ ideal for use as high-density optical memory devices, and the memory density is several hundred times greater than that of conventional devices.

To intrinsically understand the origin of the photo-induced performance of Ti$_3$O$_5$, LIU et al [68] investigated the differences among the optical properties of materials using the DFT method. Results indicated that $\lambda$-Ti$_3$O$_5$ and $\beta$-Ti$_3$O$_5$ exhibited high variance across the visible spectrum in terms of absorption and reflectivity properties. The hard X-ray photo-electron spectroscopy results indicated that some satellites can be found in both the O and Ti spectra. These phenomena could arise not because of charge-transfer excitations but valence plasmon excitations [69]. To gain more insight into the mechanism, a time-resolved diffusion reflection technique was used to study the dynamic process of this phase transition. There is a threshold for the photo-induced phase transition from $\beta$ to $\lambda$, and it begins within a few hundred femto-seconds with a non-thermal process [70]. The already formed $\lambda$-phase domains increased with a prolonged irradiation time, and a permanent phase transition was achieved when the particles were sufficiently large. Furthermore, the phase transition time induced by nano-second-pulsed or continuous-wave laser was estimated by a combination of single-shot time-resolved reflectivity measurements and Raman spectroscopy technologies. The reversible phase transition under nano-second pulse occurred at nano-second time scale ($\lambda$→$\beta$: 900 ns; $\beta$→$\lambda$: 20 ns); however, the $\lambda$ to $\beta$ transition under continuous-wave laser occurred at milli-second scale [71].

The aforementioned studies obtained several important findings, which provide novel insights into the photo-induced reversible properties of $\lambda$ and $\beta$ phases. However, all results were observed through indirect methods. After that, TASCA et al [72] directly observed the photo-induced process in structure with the excitation of a pulsed laser using a time-resolved powder XRD technique. A phase transition from $\beta$ to $\lambda$ with a time faster than the experimental time resolution (10 $\mu$s) occurred, followed by a relaxation time of 20 $\mu$s. In 2021, MARIETTE et al [73] performed a more precise and complete characterization of this process using femto-second powder XRD, as shown in Fig. 9. They suggested that the photo-induced phase transition between $\lambda$ and $\beta$ phases was initiated by the propagation of elastic deformations rather than the initial nucleation and growth process. The stress caused by structural changes led to a strain wave that traveled at the speed of sound, eventually leading to the photo-induced phase transition.

![Fig. 9](image)

**Fig. 9** (a) Experimental setup of time-resolved powder X-ray diffraction (XRD); (b) Relative intensive change of XRD patterns at different time scales; (c) Rietveld refinement results of XRD patterns for laser off and $t$=7.5 ps [73]. Reproduced with permission. Copyright 2021, Nature

### 4.4 Catalyst support

In recent years, the application of titanium sub-oxides, such as Ti$_4$O$_7$, Ti$_6$O$_{11}$ and Ti$_8$O$_{15}$, in chemical catalysts has been extensively studied due to their excellent performance in electrical conductivity, corrosion resistance and high-temperature stability [74–79]. Similarly, Ti$_3$O$_5$ also exhibits tremendous potential for use in electrode and catalyst support materials owing to its better electro-chemical activities and stability towards strong acids and bases [80].
Some researchers have discovered the potential application of Ti$_3$O$_5$ when they introduce Ti$_3$O$_5$ as catalyst support for fuel cells for cathodic oxygen reduction [81−84]. ALIPOUR MOGHADAM ESFAHANI et al [85] synthesized Ti$_3$O$_5$−Mo carbon-free support for platinum-based catalyst proton exchange membrane fuel cells (PEMFCs), as shown in Fig. 10. Significant high catalyst activity of 73 mA/mg (Pt) at a current density of 1.1 mA/cm$^2$ and 0.9 V was observed for Mo-doped Ti$_3$O$_5$, followed by that of commercial Pt/C catalyst support [86,87]. The enhanced catalyst activity was due to the combined effect of oxygen vacancies and Ti$^{3+}$ defects in Ti$_3$O$_5$. Stability and durability were also significantly improved compared to commercial Pt/C from the results of potential cycling and ultraviolet-visible (UV-Vis) measurements of electrolytes. After that, they introduced Mo and Si into Ti$_3$O$_5$ (Ti$_3$O$_5$Mo$_{0.2}$Si$_{0.4}$), showing improved performance compared with previous results (1.57 mA/cm$^2$ at 0.9 V) [29,88]. Recently, ALIPOUR MOGHADAM ESFAHANI et al [89] have introduced N-functional groups into Ti$_3$O$_5$−Mo to improve catalyst activity and stability. To ensure catalyst activity, they further investigated the durability of Pt/Ti$_3$O$_5$Mo$_{0.2}$Si$_{0.4}$ using multiple accelerated stress tests and found that the support not only stabilizes the catalyst but also ensures the effectiveness of active sites [90].

In addition to its application in PEMFCs, Pt/Ti$_3$O$_5$Mo$_{0.2}$Si$_{0.4}$ could be extended to direct methanol fuel cells (DMFCs). Excellent activities were found in methanol oxidation reactions, which were the major reaction in anodes of DMFCs [91]. A significantly higher current density of 58.92 mA/cm$^2$ was observed for Pt/Ti$_3$O$_5$Mo$_{0.2}$Si$_{0.4}$, followed by those of Pt/C catalysts. In addition, the activation energy for related reactions considerably decreased, simultaneously showing higher exchange current densities.

SHI et al [92] prepared Ti$_4$O$_7$−$\lambda$-Ti$_3$O$_5$ dual-phase nano-fibers using the hydro-thermal reaction method and used them in the oxygen reduction reaction. Ti$_4$O$_7$ and $\lambda$-Ti$_3$O$_5$ in this structure exhibit mutual synergies in catalytic activity compared with the single-phase, providing a new idea for developing electrocatalysts. This material showed good performance in terms of methanol tolerance and cyclic stability. However, electrocatalytic performance should be further improved.

4.5 Photocatalysis

Titanium suboxides, such as Ti$_2$O$_3$, Ti$_3$O$_5$, Ti$_4$O$_7$, and Ti$_8$O$_{15}$, exhibit certain photo-activities due to existence of oxygen vacancies [13,93−96]. STEM et al [97] synthesized micro-scale Ti$_3$O$_5$ on silicon substrates using carbon-doped TiO$_2$ thin films as a precursor, and the schematic illustration of prepared micro-scale meshes is shown in Fig. 11. Under visible light, it showed better absorbance and photo-luminescence emission performance due to defects within Ti$_3$O$_5$, introduced by doped carbon. Using the same method, they also prepared Ti$_3$O$_5$ thin film containing 75 wt% $\lambda$-Ti$_3$O$_5$, 25 wt% TiO$_2$ (rutile) and trace TiO$_2$−$x$C$_x$ and it is expected to be useful in solar cells and photo-catalysis [98].

QI et al [99] reported Ti$_3$O$_5$ as a catalyst for photo-degradation. Ti$_3$O$_5$ nano-rods were obtained by treating Ti$_5$Si$_3$ powders in O$_2$ flow at 800 °C for 90 min. Under the UV-Vis condition, the Ti$_3$O$_5$ nano-rods showed a good degradation effect towards methylene blue solutions, and the degradation rate could reach up to 80.0% [99].

4.6 Superconductivity

Excellent superconductivity performance was found by YOSHIMATSU et al [100] in $\gamma$-Ti$_3$O$_5$ thin films, with the highest super-conducting transition temperature of 7.1 K among simple oxides. These thin films were prepared using PLD method on
different substrates, and their properties were considerably influenced by the atmosphere around the substrates. The superconductivity properties were attributed to bipolaronic superconductivity, which has much to do with oxygen non-stoichiometry and epitaxial stabilization. After that, they investigated in more depth the mechanism of superconductivity performance of $\gamma$-Ti$_3$O$_5$ by regulating the structure phase transformation [19]. A superconducting phase diagram containing TiO, Ti$_2$O$_3$ and $\gamma$-Ti$_3$O$_5$ was created on the basis of the experimental results to clarify the superconducting state arising from $\gamma$-Ti$_3$O$_5$.

FAN et al [20] grew a series of Ti$_3$O$_5$ thin films on $\alpha$-Al$_2$O$_3$ substrates using the PLD method by controlling oxygen pressure (from $4 \times 10^{-4}$ to $1 \times 10^{-3}$ Pa). $\gamma$-Ti$_3$O$_5$ was prepared when the oxygen concentration reached $1 \times 10^{-3}$ Pa. However, no superconductivity phenomenon was found, as shown in Fig. 12 [20]. Thus, further experiments need to be conducted to investigate the detailed mechanisms.

4.7 Other application

Excellent microwave absorption performance was observed in $\lambda$-Ti$_3$O$_5$ and Li-doped $\lambda$-Ti$_3$O$_5$ due to the multivalent characteristic of Ti ions [101]. Three Ti ions with different valence states formed different micro-electric fields in the materials, which will improve the microwave absorption performance in a broad frequency range. Thus, the as-prepared $\lambda$-Ti$_3$O$_5$ showed a higher efficient absorption bandwidth than most of the other oxide-based microwave absorbing materials. In addition, Li-doped $\lambda$-Ti$_3$O$_5$ showed the highest $E_{AB}/d$ values ($E_{AB}$ is the effective absorption bandwidth; $d$ is the sample thickness) due to the formation of the Li–O micro-electric field.

LI et al [102] synthesized $\gamma$-Ti$_3$O$_5$ by hydrogen reduction of hierarchical micro-spheres of TiO$_2$, as shown in Fig. 13, and used it as the substrate of surface-enhanced Raman scattering (SERS). The as-prepared substrate exhibited a lower limit of detection ($10^{-10}$ mol/L) for Rhodamine 6G and...
excellent stability performance under conditions of high-temperature oxidation and concentrated alkali and acid with a high specific area of 405.8 m²/g. In addition, it still showed good SERS activity after several cycles of use. Compared with TiO₂ substrates, γ-Ti₃O₅ had improved detection sensitivity as high as 10000-fold.

DING et al [103] synthesized Ti₃O₅/Ti₄O₇ nano-fibers by hydro-thermal method and used them as adsorbents to capture SARS-CoV-2b (severe acute respiratory syndrome coronavirus 2) for further detection or to scavenge it from the environment. These dual-phase adsorbents exhibited a high affinity for proteins or phospholipids. Compared with Ti₆O₁₁, they showed improved adsorption and efficient performance with lower virus concentrations after adsorption. This study provided a new way for practical applications of Ti₃O₅.

5 Summary and perspective

Over a couple of decades, a considerable research effort has gone into the crystal structure, preparation methods, physical and chemical properties and applications of Ti₃O₅. There has been an exhaustive understanding of different Ti₃O₅ crystalline forms (α, β, γ, δ and λ) in terms of physical and chemical properties, and the change in physical properties that have resulted from phase transitions between these forms. Such properties confer Ti₃O₅ potential interest for use in gas sensors, photo-catalysis, catalyst support, superconductivity, etc. Especially, the unique pressure–heat, pressure–light and pressure–current reversible phase transitions between λ- and β-Ti₃O₅ with different external stimulations have been piquing increasing research interest. These also offer new applications of Ti₃O₅ in the field of energy utilization and conversion.

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的合成、性能及应用研究进展

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摘 要：自 20 世纪 50 年代以来，人们对 Ti3O5 的晶体结构、物理、化学和相变性质进行了大量研究。不同晶体结构 Ti3O5 (α、β、γ、δ 和 λ) 的性能各异，特别是 λ 与 β 相之间独特的可逆相变现象吸引了越来越多的研究兴趣，这也为 Ti3O5 在能源和数据存储领域开辟了新的应用。近年来，Ti3O5 材料在痕量检测、微波吸收和病毒吸附等方面的优异表现，进一步拓宽了其应用领域。本文详细介绍不同晶体结构 Ti3O5 的基本性质，并对其制备方法和应用领域的研究进展进行了系统的综述。

关键词：Ti3O5；相变；压力诱导；数据存储；催化剂载体

(Edited by Wei-ping CHEN)