# Ultra-High Temperature Calcination of Crystalline $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Its Nonlinear Optical Properties for Ultrafast Photonics

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As a typical transition metal oxide,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has garnered significant attention due to its advantages in nonlinear optical applications, such as strong third-order nonlinearity and fast carrier recovery time. To delve into the nonlinear optical properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials with different microstructures are prepared. The nonlinear optical features of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> calcined at the previously unexplored ultra-high temperature of >1100°C are emphasized. It is found that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> exposed to ultra-high temperatures undergoes the phase transition, leading to the formation of  $Fe_3O_4$ . Subsequently, the nonlinear absorption coefficient is measured as -0.6280 cm GW<sup>-1</sup> at 1.5  $\mu$ m. The modulation depth and saturation intensity for the Fe<sub>2</sub>O<sub>3</sub>-based saturable absorber at 1.5  $\mu$ m are 4.20% and 13.94 MW cm<sup>-2</sup>, respectively. Ultimately, the incorporation of the Fe<sub>2</sub>O<sub>3</sub>-based saturable absorber into an Er-doped fiber laser cavity resulted in the achievement of both conventional soliton mode-locking operation with a central wavelength of 1560.3 nm and a pulse duration of 1.13 ps, as well as the dissipative soliton resonance mode-locking operation with a central wavelength near 1564.0 nm. Overall, the phase transition and the nonlinear optical features in iron oxides under ultra-high temperatures are revealed, indicating the great potential in advanced ultrafast photonic applications.

## 1. Introduction

Nonlinear optical (NLO) materials are crucial components in various optoelectronic devices, with their performance often dictating the overall efficacy of these devices. In recent years, transition metal oxides (TMOs) have emerged as premier candidates for nonlinear optoelectronics due to their advantageous properties, including strong third-order nonlinearity, ultrafast carrier

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recovery time, broad absorption bandwidth, strong light-matter interaction, and elevated exciton binding energy.[1-14] Among TMOs, Fe<sub>2</sub>O<sub>3</sub> has garnered significant attention owing to its natural abundance and exceptional thermochemical stability. There exist four crystalline forms of  $Fe_2O_3$ :  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\beta$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub>.<sup>[15]</sup> Notably, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is an *n*-type semiconductor characterized by a bandgap of 2.1 eV and a rhombohedral corundum structure, recognized as the most stable form of iron oxide.[16,17] It exhibits complex magnetic behavior that includes antiferromagnetism alongside weak ferromagnetism. Furthermore, due to its low cost and environmental friendliness, it has been widely applied in catalysis,<sup>[18,19]</sup> water treatment,<sup>[20]</sup> electrochemistry,<sup>[21,22]</sup> water splitting,<sup>[23,24]</sup> nonlinear optics,<sup>[25–27]</sup> and other fields. Thanks to the wide application of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material, to date, numerous synthesis methods have been reported for producing  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material, including sol-gel method,<sup>[28]</sup> hydrothermal synthesis method,<sup>[29]</sup> solvothermal

method,  $^{[30]}$  in situ synthesis method,  $^{[31]}$  template-based method,  $^{[32]}$  and electrochemical anodization method.  $^{[33]}$ 

Generally speaking,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is frequently prone to lose surface oxygen atoms when undergoing heat treatment or chemical reactions during the preparation process, forming oxygen vacancy (O<sub>V</sub>) defects.<sup>[34,35]</sup> These oxygen vacancy defects will cause the Fe/O ratio of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to increase, enabling  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material to have more surface active sites and ultimately enhance its performance in catalysis, electrochemistry, and ultrafast photonics.<sup>[36-41]</sup> Therefore, it is of great significance to regulate the concentration of  $O_V$  in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material. To achieve this goal, people usually adjust the oxygen vacancy concentration and Fe/O ratio in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material by controlling certain parameters during the preparation process, such as the preparation temperature and holding time. Nevertheless, the aforementioned methods for preparing  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material often have drawbacks like high-cost, low yield, complex procedures, and poor controllability of oxygen vacancy concentration when preparing the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material with adjustable oxygen vacancy concentration, which restricts the large-scale production and application of modified  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material. As we all know, the high-temperature calcination method is a simple and low-cost process to prepare oxygen vacancy defects.

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**Figure 1.** a) The cell diagram of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material annealed at ultra-high temperature; b) The bader charge difference between  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at room temperature and annealed at ultra-high temperature.

During the high-temperature calcination, the lattice oxygen on the material's surface is prone to loss, thereby forming oxygen vacancy defects.<sup>[34,42,43]</sup> It is easy to regulate the concentration of oxygen vacancy and the Fe/O ratio in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material by controlling the calcination temperature and duration of the calcination process of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material. Additionally, by adjusting the calcination temperature and duration, the crystallinity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material can also be regulated. Furthermore, due to the existence of various iron oxides with different Fe/O ratios, hightemperature calcination may also cause phase transition among iron oxides, which is also beneficial for the improvement of ultrafast nonlinear optical properties.

Herein, FeOOH material was employed as the precursor, and a series of crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials with diverse microstructures were fabricated via the high-temperature calcination method at different calcination temperatures. In addition, these  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials were characterized and tested for nonlinear optical properties. Based on the characterization results, it was discovered that when the calcination temperature exceeds 1000 °C, the calcination products encompass not only  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> but also a portion of Fe<sub>3</sub>O<sub>4</sub>. Based on the results of nonlinear optical properties testing, we chose to focus on the calcined product with the calcination temperature of 1100 °C (named  $Fe_2O_3$ -H). The nonlinear absorption coefficient is -0.628 cm GW<sup>-1</sup> by utilizing a home-built Z-scan setup in the waveband of 1.5 µm. The modulation depth and saturation intensity of the Fe<sub>2</sub>O<sub>3</sub>-H saturable absorber (SA) at 1.5  $\mu$ m were 4.20% and 13.94 MW cm<sup>-2</sup> with a home-built I-scan setup. Finally, the Fe<sub>2</sub>O<sub>3</sub>-H SA was incorporated into the Er-doped fiber laser cavity to achieve the conventional soliton mode-locking operation with a central wavelength of 1560.3 nm and a pulse duration of 1.13 ps, and the dissipative soliton resonance mode-locking operation with a central wavelength near 1564.0 nm, respectively. The experimental results demonstrate that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials calcined at ultrahigh temperatures possess excellent nonlinear optical properties and great application potential in ultrafast photonics. This work paves the way for the investigation of the phase transition of iron oxides at ultra-high temperatures and their applications in the field of nonlinear optics, which will be beneficial for the future application of iron oxides in advanced ultrafast photonics and optoelectronics.

## 2. Results and Discussion

#### 2.1. DFT Simulation

In order to better understand the influence of ultra-high temperature calcination on the electronic properties and phase transitions of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials, we used VASP to perform first-principle calculations and study the difference between the electron gain and loss of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at ultra-high temperature and at room temperature, as shown in **Figure 1**. In Figure 1a, we show the cell diagram of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material after ultra-high temperature annealing. In Figure 1b, we observe that some Fe atoms in a cell of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material undergo different electron transfers after ultra-high temperature calcination. This result suggests that a part of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> may undergo the phase transition at ultra-high temperatures, leading to the formation of different iron oxide phases. In addition, the observed electron transfer may have an important effect on the nonlinear optical properties of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material, which needs to be verified experimentally.

#### 2.2. Characterization of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Materials

A series of crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials with different calcination temperatures were prepared by the high-temperature calcination method. The specific preparation process is shown in "Experimental Section." During the preparation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials through high-temperature calcination, the FeOOH precursor was annealed within a range of temperatures, and a series of calcined products with diverse microstructures were obtained. It is notable that when the calcination temperature exceeds 1000 °C, the calcined products demonstrate entirely different characteristics: First, the color of the calcined products is no longer the reddish-brown exhibited by other products, but rather shows a dark blue performance. Meanwhile, they also exhibit strong magnetism not possessed by other calcined products, which has not been reported in previous studies. The characterization results related to the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials are shown in Figure 2 and Supporting Information.

The scanning electron microscope (SEM) images of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials are shown in Figure 2a. It can be noticed that the appearance and size of the obtained  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials also







**Figure 2.** a) SEM images of calcined  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials at different calcination temperatures; b) UV–vis–IR absorption spectra of different  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials; c) Mossbauer spectroscopy of Fe<sub>2</sub>O<sub>3</sub>-H material; d) XRD patterns of different  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials; e) XPS spectra of Fe<sub>2</sub>O<sub>3</sub>-H material.

vary with the alteration of the calcination temperature. When the calcination temperature is 500 °C, the calcined  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material manifests an irregular porous flocculation structure. The formation of the porous structure can be accounted for as follows: During the high-temperature calcination process, the removal of hydroxyl groups and water causes the collapse and reorganization of the FeOOH structure, ultimately resulting in the emergence of the porous structure in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material.<sup>[41–47]</sup> When the calcination temperature is 800 °C, the obtained  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material appears as irregularly dispersed particles with a particle size of  $\approx$ 300 nm. With the increase of the calcination temperature, the particle size of the calcined products will continue to grow, which can be attributed to the growth, aggregation, and fusion of the dispersed particles after calcination at a higher temperature,<sup>[46,48]</sup> as well as demonstrated by the calcined products obtained at 1000 °C. When the calcination temperature is greater than 1000 °C, the aggregation and fusion of particles in the calcination products become more pronounced, leading to the continuous increase of the single particle volume and the continuous decrease of the single particle surface area. Figure S1 (Supporting Information) displays the microstructure images of Fe<sub>2</sub>O<sub>3</sub>-H material obtained at an ultra-high calcination temperature of 1100 °C. The SEM images of the Fe<sub>2</sub>O<sub>3</sub>-H material are depicted in Figure S1a,c (Supporting Information). It can be observed that the Fe<sub>2</sub>O<sub>3</sub>-H material exhibits an uneven block structure, with a micron-sized scale and mutual aggregation among the blocks. The transmission electron microscope (TEM) images of Fe<sub>2</sub>O<sub>3</sub>-H material are shown in Figure S1b,d (Supporting Information). In Figure S1b (Supporting Information), the homogeneous internal structure of the irregular block can be seen, while in the high-resolution transmission electron microscopy (HRTEM) image shown in Figure S1d (Supporting Information), a lattice spacing of 2.75 Å, corresponding to the (104) lattice plane of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material, can be observed, illustrating the good crystallism of the Fe<sub>2</sub>O<sub>3</sub>-H material.

Figure 2b presents the absorption spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials within the range of 200–2000 nm. It can be observed that all of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials possess broadband absorption characteristics in the near-infrared wavelength range. Nevertheless, the absorption of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials obtained through calcination at ultrahigh temperatures is significantly stronger than that of other  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials in the near-infrared band, suggesting the positive modification effect of ultra-high temperature calcination on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials in the field of nonlinear optics. Additionally, it can also be noted that the absorption spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials resulting from ultra-high temperature calcination are similar, and the absorption spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials with calcination temperatures less than 1000 °C are also mutually similar. Concurrently, the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials obtained at the calcination temperature below 1000 °C appear reddish-brown and have no strong

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Table 1. Mossbauer spectroscopy test results.

-	IS[mm/s]	QS[mm/s]	H[T]	Area[%]
Sextet(1)	0.353	-0.33	53.82	26.2
Sextet(2)	0.553	0.17	52.68	13.2
Sextet(3)	0.343	-0.26	51.79	60.6

magnetism, while the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials obtained through ultrahigh temperature calcination show dark blue and have strong magnetism. Combined with our calculation results, we hypothesize that apart from the production of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, other iron oxide materials may also emerge during the ultra-high temperature calcination process, which has not been reported in previous studies. In Figure S2 (Supporting Information), the absorption spectrum of Fe<sub>2</sub>O<sub>3</sub>-H material is provided, and the illustration is the macroscopic diagram of Fe<sub>2</sub>O<sub>3</sub>-H material. Furthermore, the spectral line jitter near the wavelength of 400 nm is caused by the change of the lamp in the test instrument.

To explore the material composition of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials obtained under ultra-high temperature calcination, we conducted the Mossbauer spectroscopy for Fe2O3-H material, and the result is presented in Figure 2c. Mossbauer spectroscopy is a frequently employed method for investigating the local magnetic behavior of Fe atoms in materials and their oxidation states. As can be seen from Figure 2c, the  $Fe_2O_3$ -H material exhibits three sextet states, demonstrating the existence of other iron oxides apart from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in the material. According to the test results of the Mossbauer spectroscopy (as shown in Table 1), for the third sextet with the highest proportion, the value of its quadrupole splitting (QS,  $-0.26 \text{ mm s}^{-1}$ ) indicates that the material possesses weak ferromagnetism. The value of its isomer shifts (IS, 0.343 mm s<sup>-1</sup>) and the value of its hyperfine field (B<sub>hf</sub>, 51.79 T) all correspond to the hematite phase,<sup>[49]</sup> which is consistent with our previous analysis results. Additionally, for the remaining two sextet states, their corresponding IS values are 0.353 and 0.553 mm s<sup>-1</sup> respectively, corresponding to Fe<sup>3+</sup> ions and Fe<sup>2+</sup> ions.<sup>[50,51]</sup> The ratio of the two is  $\approx 2.1$ , which is in accordance with the ratio of Fe<sup>3+</sup> ions to Fe<sup>2+</sup> ions in Fe<sub>3</sub>O<sub>4</sub>. Simultaneously, since at ultra-high temperatures, Fe<sub>2</sub>O<sub>3</sub> may decompose to generate  $Fe_3O_4$  and  $O_2$ . Therefore, we conclude that the  $Fe_2O_3$ -H material should contain  $Fe_3O_4$  in addition to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. This also explains the reason why the Fe<sub>2</sub>O<sub>3</sub> materials under ultra-high temperature calcination change color and demonstrate strong magnetism.

In order to investigate the impact of calcination temperature on materials' crystallinity,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials prepared were characterized by X-ray diffraction (XRD), and the results are displayed in Figure 2d. It can be perceived that the diffraction peaks of all materials correspond to the standard diffraction pattern of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDS#89-0597). Meanwhile, when the temperature is lower than 1000 °C, the crystallinity of the materials improves with the increase of calcination temperature. This is also manifested by the fact that the peak at  $2\theta = 33.1^{\circ}$  becomes sharper and more intense. All these phenomena suggest that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystal grains grow significantly with the increase of calcination temperature, leading to better crystallinity. Additionally, when the temperature is higher than 1000 °C, the crystallinity of the calwww.advancedscience.com

cined products deteriorates. The possible causes are as follows: A part of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials decompose at ultra-high temperatures, and the ultra-high temperature environment will also damage the original crystal structure of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials, resulting in poorer crystallinity. The XRD characterization result of Fe<sub>2</sub>O<sub>3</sub>-H material was presented in Figure S3 (Supporting Information), and it can be observed that the Fe<sub>2</sub>O<sub>3</sub>-H material is polycrystalline. The peak at  $2\theta = 33.1^{\circ}$  corresponds to the (104) lattice plane of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which is in accordance with our previous HRTEM result. It is worth noting that the presence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can only be determined through the XRD pattern of the Fe<sub>2</sub>O<sub>3</sub>-H material. The reason for this phenomenon is elucidated as follows: During the materials preparation process at ultra-high temperatures, Fe<sub>3</sub>O<sub>4</sub> may form fewer crystals or exist as a short-range ordered phase along the hematite crystals, thereby not presenting significant peaks in the XRD pattern.<sup>[49]</sup>

We also found that Fe<sub>2</sub>O<sub>3</sub>-H material undergoes the phase transition at ultra-high temperatures, and has the best crystallinity after calcination at ultra-high temperatures. In order to further investigate the Fe<sub>2</sub>O<sub>3</sub>-H material, X-ray photoelectron spectroscopy (XPS) was employed and the results are presented in Figure 2e. It can be observed that the Fe 2p energy spectrum predominantly exhibits two asymmetric peaks, corresponding respectively to the Fe  $2p_{1/2}$  peak and Fe  $2p_{3/2}$  peak, with their binding energies concentrating at  $\approx$ 724 and 710 eV. Each asymmetric peak can be decomposed into two fitting peaks, among which the one with the higher binding energy pertains to Fe<sup>3+</sup> ions, and the one with the lower binding energy pertains to Fe<sup>2+</sup> ions.<sup>[52,53]</sup> Additionally, the two peaks of binding energy concentrating at  $\approx$ 732 and 719 eV respectively correspond to the satellite peaks of Fe  $2p_{1/2}$  peak and Fe  $2p_{3/2}$  peak.<sup>[54]</sup> As the Fe<sub>2</sub>O<sub>3</sub>-H material is fabricated by the high-temperature calcination method, and during the material calcination process,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material readily loses the oxygen atoms on the surface to form oxygen vacancy, resulting in a certain amount of oxygen vacancy defects on the surface of the Fe<sub>2</sub>O<sub>3</sub>-H material. The formation of oxygen vacancy on the surface will also induce the formation of Fe<sup>2+</sup> ions on the surface, as depicted in the following equation:  $2Fe^{3+} \rightarrow 2Fe^{2+} +$ O<sub>v</sub>. This leads to a significant proportion of Fe<sup>2+</sup> ions in the XPS analysis results used to detect the valence states of elements on the surface of  $Fe_2O_3$ -H material. In addition, the O 1s energy spectrum can be decomposed into three principal peaks, where the peak at  $\approx$ 529.2 eV is associated with lattice oxygen (O<sub>1</sub>), the peak at  $\approx$ 531.5 eV corresponds to oxygen vacancy, and the peak at  $\approx$ 535.0 eV can be attributed to chemisorbed oxygen (O<sub>C</sub>).<sup>[55,56]</sup> To verify the influence of calcination temperature on material composition and elemental valence states, XPS tests were carried out on all calcined products, and the fitting results were summarized in Table S1 (Supporting Information). By analyzing the data, it is found that the content of Fe<sup>2+</sup> ions decreases and the content of O<sub>V</sub> decreases with the increase of calcination temperature below 1000 °C. In combination with the SEM images shown in Figure 2a, the reason might be that with the increase of calcination temperature, the particle size of the materials becomes larger and the surface area becomes smaller, thereby the oxygen vacancy formed by the loss of oxygen atoms from the surface becomes less. When the calcination temperature is greater than 1000 °C, the  $O_V$  content of the material remains essentially unchanged, while the Fe<sup>2+</sup> ions content increases with the increase





**Figure 3.** a) The schematic diagram of the in-line balanced twin-detector system; b) Nonlinear transmission curve of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material calcined at 900 °C; c) Nonlinear transmission curve of Fe<sub>2</sub>O<sub>3</sub>-H material; d) Nonlinear transmission curve of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material calcined at 1300 °C.

of the calcination temperature, indicating that the reaction of  $Fe_3O_4$  formation becomes more intense with the increase of temperature under an ultra-high temperature environment.

#### 2.3. Nonlinear Optical Response

#### 2.3.1. In-Line Balanced Twin-Detector System

According to the comprehensive characterization analysis, the Fe<sub>2</sub>O<sub>2</sub>-H material exhibits stronger absorption in the nearinfrared band when compared to the conventional  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials without phase transition. Notably, among the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials subjected to ultra-high temperatures, the Fe<sub>2</sub>O<sub>3</sub>-H variant demonstrates the superior crystallinity during the phase transition. To explore whether the phase transition of materials has any influence on the nonlinear optical properties of  $\alpha$ -Fe<sub>2</sub>O<sub>2</sub> materials, we selected three types of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> obtained by calcination at 900, 1100, and 1300 °C to measure the nonlinear optical properties, and the results are depicted in Figure 3. In Figure 3a, we constructed an in-line balanced twin-detector system, and the specific parameters of the system and the SAs used in this system are provided in the "Experimental Section." In Figure 3b-d, it can be observed that when the excitation intensity employed is low, the light absorption of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials gradually reduces as the excitation intensity increases. At higher excitation intensity, the absorption tends to be saturable. The saturable absorption curve can be fitted with the following Equation (1):<sup>[57]</sup>

$$T = 1 - \Delta T \times \exp\left(\frac{-I}{I_{sat}}\right) - \alpha_0 \tag{1}$$

where *T* is the light transmittance,  $\Delta T$  is the modulation depth, *I* is the excitation intensity,  $I_{sat}$  is the saturation intensity, and  $\alpha_0$  is the unsaturated loss. From Figure 3b–d, it is evident that the modulation depth of Fe<sub>2</sub>O<sub>3</sub>-H material is 4.20%. Additionally, the saturation intensity of Fe<sub>2</sub>O<sub>3</sub>-H material is 13.94 MW cm<sup>-2</sup>.

To demonstrate the superior performance of Fe<sub>2</sub>O<sub>3</sub>-H material as SA, we have included the performance comparison between Fe<sub>2</sub>O<sub>3</sub>-H material and other materials in the Supporting Information. As can be seen from the Table S2 (Supporting Information), Fe2O3-H material exhibits a large modulation depth and low saturation intensity compared to other materials, highlighting its significant potential for practical applications as SA. The enhancement of the nonlinearity would be ascribed to the strong quantum confinement and local field effects from dielectric confinement and saturable excitonic resonance. Therefore, under laser irradiation, in the Fe<sub>2</sub>O<sub>3</sub> materials undergoing a phase transition, more photons are needed to reach the bleached state, leading to the nonlinear absorption coefficient and enhanced nonlinearity. It is noting that under high excitation intensity, Fe<sub>2</sub>O<sub>3</sub>-H material exhibits reverse saturable absorption (RSA), as shown in the illustration in Figure 3c. When the excitation intensity surpasses 400 MW cm<sup>-2</sup>, the transmittance of Fe<sub>2</sub>O<sub>3</sub>-H SA decreases by 0.57%. We attribute the RSA effect may be caused by the two-photon absorption (TPA) effect,<sup>[58,59]</sup> which contributes favorably to achieving high-energy dissipative soliton resonance mode-locking operation. However, with the calcination temperature increasing, the lattice structure deteriorates and crystallization quality diminishes, leading to structural defects that may reduce the nonlinearity of these Fe<sub>2</sub>O<sub>3</sub> materials, as shown in Figure 3d.



**Figure 4.** Conventional soliton mode-locking operation of  $Fe_2O_3$ -H material. a) The output power and single pulse energy vary with pump power; b) Pulse train; c) Optical spectrum; d) Autocorrelation trace; e) RF spectrum; f) RF spectrum within a span of 0–1 GHz.

#### 2.3.2. Open-Aperture Z-Scan System

From the aforementioned I-scan experimental results, we established that the Fe<sub>2</sub>O<sub>3</sub>-H material exhibits superior nonlinear optical performance as SA at 1.5 µm. To further investigate the nonlinear performance of Fe<sub>2</sub>O<sub>3</sub>-H material comprehensively, we employed an open-aperture Z-scan system to measure the effective nonlinear absorption coefficient ( $\beta_{eff}$ ) of these  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials, as illustrated in Figure S4 (Supporting Information). Figure S4a (Supporting Information) shows the experimental setup of the open-aperture Z-scan system used. The nonlinear polarization rotation mode-locking fiber laser, which is identical to the in-line balanced twin-detector system, serves as the laser source of the open-aperture Z-scan system. After the pulse laser is amplified by an Er-doped fiber amplifier, it traverses a focusing lens with a focal length of 50 mm and a quartz plate coated with prepared Fe<sub>2</sub>O<sub>3</sub>-H material and is eventually received by the detector. Throughout the experiment, various power values can be attained by continuously adjusting the position of the quartz plate on the slide rail. The corresponding Z-scan curve can be acquired by fitting the experimental data. The Z-scan curve can be fitted with the following Equation (2):[60]

$$T = \sum_{m=0}^{\infty} \frac{\left[-q_0(z,0)\right]^m}{(m+1)^{1.5}} (m \in N); \quad q_0(z,0) = \frac{\beta_{eff} \cdot L_{eff} \cdot I_0}{1+z^2/z_0^2}$$
(2)

where *T* is the normalized transmittance, *z* is the relative distance of the sample on the *z*-axis with respect to the focal point of the lens,  $L_{eff}$  is the effective length of the materials,  $I_0$  is the peak laser intensity, and  $z_0$  is the Rayleigh length. In our openaperture Z-scan experiment, the beam spot diameter is  $\approx 100 \,\mu\text{m}$ , the peak laser intensity is  $\approx 203.7 \,\text{GW cm}^{-2}$ , and the effective length of the Fe<sub>2</sub>O<sub>3</sub> materials is  $\approx 40 \,\mu\text{m}$ . As can be seen from Figure S4b–d (Supporting Information), the  $\beta_{\text{eff}}$  of the Fe<sub>2</sub>O<sub>3</sub>-H material is  $-0.628 \,\text{cm GW}^{-1}$ . Compared with other Fe<sub>2</sub>O<sub>3</sub> materials, it has a larger absolute value, indicating that it has a better nonlinear absorption effect, further demonstrating the more ex-

cellent nonlinear optical properties of the  $\mathrm{Fe_2O_3}\text{-}\mathrm{H}$  material at 1.5  $\mu m.$ 

#### 2.4. Ultrafast Mode-Locking Operations

To investigate the application of the fabricated Fe<sub>2</sub>O<sub>3</sub>-H material in the domain of nonlinear optics, we established a typical Er-doped fiber resonator, as depicted in Figure S5 (Supporting Information). It employs a laser diode (LD) with an operational wavelength of 976 nm and a peak power of 450 mW as the pump source. The wavelength division multiplexer (WDM) operating at 980/1550 nm is accountable for coupling the pump light and the signal light into the same fiber. A polarization-independent isolator (PI-ISO) guarantees the one-way transmission of the laser within the cavity. The polarization controller (PC) is utilized to regulate the polarization state. An optical coupler (OC) with a 10% tap ratio at 1550 nm outputs 10% of the signal light and enables the remaining light to continue oscillating within the cavity. The 1.2-m-long Er-doped fiber (EDF, Fibercore I-25) serves as the gain fiber of the resonator, and its group velocity dispersion (GVD) is 40  $ps^2$  km<sup>-1</sup>. Additionally, the devices within the cavity are connected by the single-mode fiber (SMF, SMF-28e), with a GVD of  $-22.3 \text{ ps}^2 \text{ km}^{-1}$  and a total length of 29.4 m. Consequently, the total length of the utilized ring resonator is 30.6 m, and a total abnormal dispersion within the cavity is -0.608ps<sup>2</sup>. It is notable that when there is no SA in the resonator, the ultra-short pulse output cannot be achieved regardless of how the output power of the pump source or the polarization state in the cavity is adjusted. This indicates that the key to achieving ultrashort pulse output resides in the self-made SA.

#### 2.4.1. Conventional Soliton Mode-Locking Operation

Initially, we incorporate the tapered fiber without the  $Fe_2O_3$  SA into the laser resonator. No mode-locking operation is observed. Then, we incorporate the SA into the laser cavity. By gradually



ramping up the pump power and meticulously adjusting the PC's state, the self-started conventional soliton mode-locking operation is achieved at a pump power of 245.8 mW, as depicted in **Figure 4**. In this case, the light with high intensities can pass the uct (T  $Fe_2O_3$  SA, while the low-intensity light is absorbed, leading to the mode-locking operation. Figure 4a illustrates the linear correlation between output power and single pulse energy with varying pump power. The increase in pump power from 245.8 to 395.8 mW results in an escalation of output power from 52.6 to 77.6  $\mu$ W, accompanied by a corresponding rise in single pulse energy in the exhibit pulse train spanning over 1.6  $\mu$ s with a pulse interval of 153.15 ns, alongside a stable pulse train covering a time span of 10  $\mu$ s, indicating the stability of mode-locking operation.

Furthermore, Figure 4c presents the spectrum of conventional soliton mode-locking operation featuring the central wavelength of 1560.3 nm and the 3 dB spectral width of 2.48 nm. The modelocking spectrum is centered at 1560 nm instead of 1530 nm, which can be attributed to the large absorption at 1530 nm, leading to the small gain. Thus the mode-locking operation at 1560 nm is easier. It also shows the clear Kelly sidebands, which is a typical feature of lasers operating under conventional soliton mode-locking operation.<sup>[61]</sup> The enhanced resonance between the dispersive wave and the soliton wave can lead to the Kelly sidebands. The Kelly sidebands are distributed symmetrically around the spectral center peak, and their space is decided by the total dispersion value of the fiber cavity. In addition, the presence of continuous light is observed at the top of the spectrum, which comes from the interaction between the birefringent effect of the fiber and the nonlinear optical properties of SA.<sup>[62,63]</sup> The autocorrelation trace displayed in Figure 4d reveals that the full width

at half-maximum (FWHM) measures at  $\approx$ 1.74 ps while hyperbolic secant fitting yields an estimated pulse duration of  $\approx$ 1.13 ps, consequently resulting in the calculated time-bandwidth product (TBP) slightly exceeding standard values at  $\approx$ 0.345. This indicates a minor chirping effect within the pulses. Additionally, as shown in Figure 4e, we can see the radio frequency (RF) spectrum with a signal-to-noise ratio (SNR) of  $\approx$ 61.8 dB, which has a center frequency of  $\approx$ 6.53 MHz, corresponding to the pulse interval of 153.15 ns. Finally, Figure 4f provides the RF spectrum in the 1-GHz range, further substantiating the excellent stability exhibited during conventional soliton mode-locking operation.

#### 2.4.2. Dissipative Soliton Resonance Mode-Locking Operation

In order to further explore the potential for mode-locking of Fe<sub>2</sub>O<sub>3</sub>-H material in the 1.5 µm band, the dissipative soliton resonance (DSR) mode-locking operation was finally achieved through continuous adjustment of both the pump power and polarization state, as illustrated in Figure 5. Figure 5a-d presents the various mode-locking results obtained at a pump power of 275.8 mW: Figure 5a displays the spectrum of DSR mode-locking operation with a central wavelength  $\approx$ 1564 nm. Figure 5b exhibits a typical pulse sequence spanning 800 ns with a pulse interval of 153.15 ns. The regular pulse sequence indicates the stability of the mode-locking state. Figure 5c shows an individual single pulse over a time span of 30 ns, featuring a pulse width of 6.45 ns. As depicted in Figure 5d, the RF spectrum is shown with an SNR approximately reaching 59 dB and a center frequency measuring at 6.53 MHz. Additionally, Figure 5e depicts the output power and pulse width as a function of pump power. As the pump

power increases from 251.8 to 299.8 mW, the output power rises from 1.64 to 2.03 mW and the pulse width rises from 5.0 to 7.4 ns. Among them, the direct visualization of the variation of pulse width with pump power is depicted in Figure 5f. With the continuous broadening of the DSR mode-locking pulse, the peak power was finally clamped at a low level of  $\approx$ 42 mW, and the pulse energy can be continuously increased, which is consistent with the characteristics of the DSR mode-locking operation.

## 3. Conclusion

In this paper, a series of crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials with different microstructures were fabricated by the high-temperature calcination method. We discovered that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material undergoes the phase transition at ultra-high temperatures, leading to the formation of Fe<sub>3</sub>O<sub>4</sub>. The phase transition resulted in their optical absorption being enhanced as indicated by the characterization results. Furthermore, the results of the nonlinear optical properties tests indicated an enhancement in the modulation depth and nonlinear absorption coefficient of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials that had undergone phase transition. This suggested that phase transition positively influenced material modification. Notably, Fe<sub>2</sub>O<sub>3</sub>-H material exhibited superior performance compared to others. The nonlinear absorption coefficient of Fe<sub>2</sub>O<sub>3</sub>-H material was measured as -0.628 cm GW<sup>-1</sup> using a home-built Z-scan setup. The modulation depth and saturation intensity of Fe<sub>2</sub>O<sub>3</sub>-H SA were determined by a home-built I-scan setup, which was 4.20% and 13.94 MW cm<sup>-2</sup>, respectively. Finally, Fe<sub>2</sub>O<sub>3</sub>-H SA was added into an Er-doped fiber laser cavity, and the conventional soliton mode-locking operation with a central wavelength of 1560.3 nm and a pulse duration of 1.13 ps, as well as the dissipative soliton resonance mode-locking operation with a central wavelength near 1564.0 nm were obtained. Based on our experimental results, the Fe<sub>2</sub>O<sub>3</sub>-H material obtained at ultra-high temperature is regarded as a superior nonlinear optical material. Our research also lays the foundation for the future development of iron oxides in advanced ultrafast photonic applications.

## 4. Experimental Section

DFT Simulation: The first-principle simulation was performed on a VASP with PAW and PBE approximation. The self-consistent convergence energy was lower than  $1 \times 10^{-6}$  eV, and the force convergence was within  $-1.5 \times 10^{-2}$  eV A<sup>-1</sup>. The cutoff energy of the plane wave was 550 eV. The accuracy of the Brillouin zone sampling (K-Mesh) was  $7 \times 7 \times 7$  with the Gamma, ensuring smooth computations. The temperature parameter is set to 1373 K.

Preparation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Materials by High-Temperature Calcination Method: A series of crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials with different calcination temperatures were prepared by the high-temperature calcination method. The process is as follows: Initially, a specific quantity of FeOOH powder (Merck Inc.) is placed in a corundum crucible and then positioned inside a muffle furnace. The temperature within the Muffle furnace was gradually increased at a heating rate of 200 °C h<sup>-1</sup>, and maintained at different final temperatures for 3 h under the air atmosphere. Subsequently, the temperature, it could get different  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials in the crucible. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material with a calcination temperature of 1100 °C was named Fe<sub>2</sub>O<sub>3</sub>-H.

The Specific Parameters of In-Line Balanced Twin-Detector System: A self-made nonlinear polarization rotation (NPR) Er-doped fiber laser

(EDFL) was used as the laser source with a central wavelength of 1534.0 nm, a repetition frequency of 11.17 MHz, and a pulse duration of 904.7 fs. The NPR mode locking fiber laser consisted of a 976 nm laser diode, a three-in-one device containing a wavelength division multiplexer, an optical coupler and isolator, a polarization controller, a polarization-dependent isolator (PD-ISO) that ensures the laser operates in the NPR mode locking state, an Er-doped fiber and a single mode fiber. In order to ensure sufficient input power when measuring the nonlinear saturable absorption of the material, a self-made Er-doped fiber amplifier (EDFA) is used to further improve the intensity of the excited laser. After the excitation laser is amplified, the input excitation laser intensity can be adjusted by a variable optical attenuator (VOA). The optical coupler with a spectral ratio of 1:1 divides the excitation laser into two equal intensity sub-beams, one of which is measured directly by the power meter (PM) as a reference light, and the other is measured by the PM as a signal light after passing through the SA

Fabrication of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> SAs: To prepare the saturable absorbers based on different  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials, the different  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials were initially thoroughly ground. Subsequently, the different ground  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powders were separately added to anhydrous ethanol solution. Then, the mixtures were subjected to ultrasonic treatment, and centrifugation was performed after the completion of the ultrasonic process. The supernatants after centrifugation were collected and reserved. Finally, the material within the supernatants was transferred to the tapered region of the homemade tapered fiber through the optical deposition method, and the requisite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> SAs could thus be obtained. Here, the tapered fiber was used has a minimum waist diameter of 12.7 µm, a tapered region length of 8.4 mm, and an original insertion loss of 46.0%.

*Characterization*: The microstructure and morphology of  $Fe_2O_3$ -H material were characterized by scanning electron microscopy (TESCAN MIRA LMS, Czech Republic) and transmission electron microscopy (JEOL JEM-F200, Japan). The absorption spectrum of the materials in the ultraviolet to near-infrared band was studied by UV–vis–NIR spectrophotometer (Shimadzu UV-3600, Japan). The material composition and valence state of the Fe element were analyzed by Mossbauer spectrometer (ms500). The X-ray diffraction pattern was provided by the X-ray diffractometer (Rigaku MiniFlex600). The X-ray photoelectron spectra of the material were obtained by X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha).

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

## **Author Contributions**

C.H. and Z.Q. designed and performed the experiments. P.H. and P.Z. performed the formal analysis. T.Q. and Z.S. helped analyze the data. C.H. and L.D. conceived the idea and co-supervised the project. All authors contributed to the general discussion.

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## **Data Availability Statement**

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

## Keywords

mode-locking, nonlinear optical properties, phase transition, ultra-high temperature,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>

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