Electron-trapping materials, due to their exceptional ability of energy storage and controllable photon release under external stimulation, have attracted considerable attention in the field of optical information storage (OIS). In this work, Gd$_3$Al$_3$Ga$_2$O$_{12}$:Ce$^{3+}$, Yb$^{3+}$ fluorescent ceramics, were developed using air and vacuum sintering technology. By co-doping Ce$^{3+}$ and Yb$^{3+}$, the trap density was significantly increased by 7.5 times compared to samples containing only Ce$^{3+}$. Vacuum annealing further enhanced trap density by 1.6 times compared to samples sintered solely in air, while generating deep traps (1.44 eV), making Gd$_3$Al$_3$Ga$_2$O$_{12}$:Ce$^{3+}$, Yb$^{3+}$ an excellent OIS medium. This work is expected to facilitate the development of OIS materials.

Keywords: electron-trapping materials; optical information storage; Gd$_3$Al$_3$Ga$_2$O$_{12}$:Ce$^{3+}$, Yb$^{3+}$; two-step sintering method.

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1. Introduction

Optical information storage (OIS) is widely regarded as one of the most promising data storage methods, primarily due to its unique advantages such as high security, long lifespan, and low energy consumption$^{[1,2]}$. Traditional OIS materials, such as azo metal chelates, cyanine dyes, and other organic dyes$^{[3,4]}$, have encountered significant challenges, including poor physicochemical stability and limited storage capacity. Electron-trapping materials (ETMs) offer unique advantages such as high security, long lifespan, and uniformity, showing great potential in the field of optical storage$^{[5,6]}$. Several studies have explored various ETMs for optical storage, including mixtures of phosphors with organic or inorganic materials such as SrSi$_2$O$_2$N$_2$:Ln$^{2+}$, Ln$^{3+}$ (Ln$^{2+}$ = Yb, Eu; Ln$^{3+}$ = Dy, Ho, Er), Y$_2$GeO$_5$:Pr$^{3+}$, Tb$^{3+}$, or SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$$^{[7-9]}$. As an optical storage medium, a higher trap density is an important indicator that directly affects the performance of information storage. However, these mixtures have a lower density of traps in the same size region compared to ceramics that are uniformly lumped. Furthermore, ceramic materials offer significant advantages, including greater stability and uniformity, showing great potential in the field of optical storage$^{[10]}$.

Gd$_3$Al$_3$Ga$_2$O$_{12}$ (GAGG) fluorescent ceramics have attracted great attention due to their outstanding optical, thermal, and mechanical properties, and have been widely used as scintillation, light-emitting diodes, and laser materials$^{[11-13]}$. However, they have hardly been applied in the field of optical storage. Given the volatility of Ga$_2$O$_3$ (one of the raw materials), ensuring the formation of a pure garnet phase during the GAGG synthesis necessitates maintaining ample oxygen$^{[14]}$. However, the presence of oxygen during sintering unavoidably diminishes the count of oxygen vacancies, which affects the trap density of this material. This contradiction limits the application of GAGG in the field of optical storage.

In this work, fluorescent ceramics Gd$_3$Al$_3$Ga$_2$O$_{12}$:Ce$^{3+}$, Yb$^{3+}$ (GAGG:Ce$^{3+}$, Yb$^{3+}$) were synthesized through a two-step sintering method (air sintering + vacuum annealing). The co-doping of Yb$^{3+}$ and Ce$^{3+}$ increases the trap density by 7.5 times compared to samples that only contain Ce$^{3+}$. Vacuum annealing further enhanced trap density by 1.6 times compared to samples sintered solely in air, while generating deeper traps (1.44 eV), making GAGG:Ce$^{3+}$, Yb$^{3+}$ an excellent information storage medium. In addition, the information storage mechanism of the Ce$^{3+}$ and Yb$^{3+}$ co-doped GAGG is explained based on energy storage and controllable photon release under external stimulation. Furthermore, we successfully demonstrated that optical information can be effectively written using a 254 nm Hg lamp and read out through both heating and optical stimulation.
2. Experiment

2.1. Preparation of ceramics

The samples of GAGG:0.002Ce<sup>3+</sup>,xYb<sup>3+</sup> (x = 0, 0.0025, 0.0030, 0.0035, 0.0040) were chemically prepared by high temperature solid-state reaction. Chemical regents include Gd<sub>2</sub>O<sub>3</sub> (99.99%), Al<sub>2</sub>O<sub>3</sub> (99.99%), Ga<sub>2</sub>O<sub>3</sub> (99.99%), CeO<sub>2</sub> (99.99%), and Yb<sub>2</sub>O<sub>3</sub> (99.99%); as shown in Fig. 1, raw materials were mixed with anhydrous alcohol according to stoichiometric ratio and ground in a planet-type ball mill at 200 r/min for 12 h. The ball-milled mixtures were rinsed with anhydrous alcohol and dried in an oven at 80°C for 6 h. Then, the dried samples were thoroughly ground. After grinding, the dried powders were sieved through a 200-mesh screen. Prior to sintering, the green bodies were shaped from powders under uniaxial press of 30 MPa and were cold-isostatic-pressed (CIP) at 210 MPa. Then, the embryos were sintered in a muffle furnace at 1600°C for 2 h under air conditions to obtain a stable GAGG garnet. After that, they were annealed at 1400°C in a vacuum sintering furnace for 2 h.

3. Results and Analysis

3.1. Structure and optical properties

Figure 2(a) shows the XRD spectra of the fluorescent ceramics of SA0, SA25, SA30, SA35, SA40, and SA35V. No obvious impurity peaks were observed, and the diffraction peaks were in good agreement with the standard XRD spectra of GAGG. This indicates that Ce<sup>3+</sup>, Yb<sup>3+</sup>, and vacuum annealing do not change the phase of the material. To obtain the detailed crystal information of the prepared samples, the SA35V was chosen representatively to implement Rietveld structure refinement by adopting the general structure analysis system (GSAS) program, as shown in Fig. 2(b). The refinement factor of weighted profile R-factor (Rwp) and the expected R-factor (Rp) are determined to be 4.85% and 3.50%, respectively, indicating that the refined results are reliable. The refinement further confirms the phase purity. As demonstrated in Table 1, Ga ions occupy both the octahedral and tetrahedral sites, agreeing well with previous results<sup>15</sup>.

To study the microstructure and elements composition of the ceramic samples, SEM and elemental mapping tests were conducted on them. As shown in the Fig. 3, the structure of the samples is uniform with few micropores and defects. The elemental mapping pictures of the sample indicate that the ceramic samples are primarily composed of Gd, Al, Ga, Ce, Yb, and O elements, and their chemical composition is evenly distributed.

As shown in Fig. 4, we tested the PLE and PL spectra of SA0, SA25, SA30, SA35, SA40, and SA35V. No obvious impurity peaks were observed, and the diffraction peaks were in good agreement with the standard XRD spectra of GAGG. This indicates that Ce<sup>3+</sup>, Yb<sup>3+</sup>, and vacuum annealing do not change the phase of the material. To obtain the detailed crystal information of the prepared samples, the SA35V was chosen representatively to implement Rietveld structure refinement by adopting the general structure analysis system (GSAS) program, as shown in Fig. 2(b). The refinement factor of weighted profile R-factor (Rwp) and the expected R-factor (Rp) are determined to be 4.85% and 3.50%, respectively, indicating that the refined results are reliable. The refinement further confirms the phase purity. As demonstrated in Table 1, Ga ions occupy both the octahedral and tetrahedral sites, agreeing well with previous results.<sup>15</sup>

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As shown in Fig. 4, we tested the PLE and PL spectra of SA0, SA25, SA30, SA35, SA40, and SA35V. As shown, all the PLE spectra contain three bands (peaks located around 275, 345 and 445 nm). The peak around 275 nm corresponds to the
$^8S_{7/2} \rightarrow ^6I_{1}$ leaps of the Gd$^{3+}$, and the other bands around 345 and 445 nm are the Ce$^{3+}$ transitions from the 4f to 5d$_1$ and 5d$_2$, respectively. As shown in the PL spectra, all the samples emit green light under light excitation at 450 nm, which is attributed to the 5d $\rightarrow$ 4f transition of Ce$^{3+}$\textsuperscript{16}.

Trap levels are critical in determining the information storage properties of ETMs. TL spectra serve as an effective tool for studying trap levels, providing information about their depths and amount. TL spectrum tests were conducted on GAGG:Ce$^{3+}$, Yb$^{3+}$ with a heating rate of 1 K/s. Prior to testing, the samples were irradiated with a 254 nm UV light for 5 min, followed by a 5-min interval to eliminate afterglow. The TL intensity was recorded while heating the sample to 673 K. As shown in Fig. 5(a), the samples were sintered only in air; the TL intensity initially increased and then decreased with increasing Yb$^{3+}$ concentration. The TL intensity reached its maximum at $x = 0.0035$. We define the TL curves area integral as the trap density, as shown in Fig. 5(b). In the sample with only Ce$^{3+}$ added, the TL was observed, but the relative intensity was weak. Then, we found that the capture density is significantly increased with the addition of Yb$^{3+}$ ($x = 0.0035$) by a factor of 7.5 compared to the sample without Yb$^{3+}$, and the peak of the TL is shifted toward higher temperature, implying deeper trap depth, consistent with findings reported in the literature\textsuperscript{17}. Significantly, the sample was sintered in air and subjected to vacuum annealing; there was a significant increase in trap density. The trap density increased by a factor of 1.6 compared to samples sintered only in air and created more deep trap defects (1.44 eV).

### Table 1. Rietveld Refined Occupancy and Coordinates ($x$, $y$, $z$) in the Gd$_3$Al$_3$Ga$_2$O$_{12}$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>24c</td>
<td>0.125</td>
<td>0</td>
<td>0.25</td>
<td>1</td>
</tr>
<tr>
<td>Ga$_1$</td>
<td>16a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.350(7)</td>
</tr>
<tr>
<td>Al$_1$</td>
<td>16a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.650(7)</td>
</tr>
<tr>
<td>Ga$_2$</td>
<td>24d</td>
<td>0.375</td>
<td>0</td>
<td>0.25</td>
<td>0.607(11)</td>
</tr>
<tr>
<td>Al$_2$</td>
<td>24d</td>
<td>0.375</td>
<td>0</td>
<td>0.25</td>
<td>0.533(11)</td>
</tr>
<tr>
<td>O</td>
<td>96h</td>
<td>0.104(27)</td>
<td>0.199(24)</td>
<td>0.290(20)</td>
<td>1</td>
</tr>
</tbody>
</table>
As shown in Fig. 6, there are two TL peaks that indicate that the sample contains two traps with different depths (T1 and T2). We used the Hoogenstraaten method to calculate the trap depth of SA35V. First, a series of TL curves was measured at different heating rates, as shown in Fig. 6. The trap depths can be calculated as the following [Eq. (1)]\(^{18}\):

\[
\beta E/k_B T_m^2 = s \exp(-E/k_B T_m),
\]

where \(E\) (eV) is the trap depth; \(\beta\) (K/s) is the heating rate; \(k_B\) is the Boltzmann constant; \(T_m\) (K) is the TL spectral peak temperature; and \(s\) (s\(^{-1}\)) is the frequency factor. By plotting \(\ln(T_m^2 = \beta/k_B T_m)\) versus \(1 = k_BT_m\), the trap depth of the TL curve can be determined from the slope of the straight line, as shown in Fig. 6. The trap depths of SA35V fits are 1.44 and 0.81 eV, respectively. According to Table 2, the trap depths are large enough to classify them as exceptional optical storage materials within typical ETMs.

### 3.2. Analysis of optical storage mechanism

The XPS was used to verify the existence of oxygen vacancies in the obtained samples. After peak fitting, it was found that the O 1s peaks of the three samples (SA0, SA35, and SA35V) could be categorized into lattice oxygen, vacancy oxygen, and surface absorbed oxygen\(^{29}\), located at 533.36–533.65, 531.74–532.02, and 530.10–530.24 eV, respectively, as shown in Fig. 7. It has been observed that the SA0 exhibits a minor presence of oxygen vacancies (pink region). Upon the addition of Yb\(^{3+}\), a notable enhancement in the relative area representing oxygen vacancy (VO) was observed in the O 1s peak. Furthermore, after vacuum annealing, the content of VO exhibited a noticeable increase. This observation aligns with the previously discussed phenomenon of progressively heightened TL intensity across the three samples.

To further investigate the trap combinations, we performed a 10-h annealing in air at 1300°C on the SA35V and SA0 samples to eliminate VO. We used EPR to detect the concentration of VO in SA0 and SA35V after air annealing. As shown in Fig. 8(b), a notable signal at \(g = 2.005\) is observed in SA35, and we interpret this signal as indicating the presence of VO\(^{30}\). Importantly, after air annealing, SA0 and SA35V exhibit no such signal, indicating the absence of VO. Therefore, we conclude that SA0 and SA35V,
after air annealing, are free of $V_{O}$. As shown in Fig. 8(a), We find that after air annealing the deeper traps of SA0 disappear entirely, while the shallow traps weaken and shift to the left. Therefore, we can speculate the presence of two types of oxygen vacancy traps in SA0. We identified two types of oxygen vacancy traps: $V_{O1}$ located in the low-temperature region and $V_{O2}$ in the high-temperature region. After air annealing, we still observed weak TL signals in SA0, which can be attributed to gallium vacancies ($V_{Ga}$)\(^{[31]}\). After annealing SA35V in air to remove oxygen vacancies, the TL signal of the deep traps vanished, while the TL intensity of the shallow traps diminished significantly but remained higher than that of SA0. Therefore, we speculate that the deep traps are mainly caused by $V_{O2}$, and the enhancement in TL intensity at the shallow traps compared to SA0 can be attributed to the independent electron capture ability of $Yb^{3+}$, which acts as an electron trap by capturing one electron and transforming it into $Yb^{2+}$. Therefore, we infer that the deep traps (T2) in the SA35V consist solely of $V_{O2}$, while the shallow traps (T1) consist of defect aggregates formed by $V_{O1}$, $Yb^{3+}$, and a small amount of $V_{Ga}$.

We proposed the optical storage mechanism of GAGG:Ce\(^{3+}\), Yb\(^{3+}\) as shown in Fig. 9. In GAGG, Ce\(^{3+}\) acts as the luminescent center and electron donor. Under 254 nm light excitation (write-in), electrons are excited from the ground state to the 5d level, generating holes in the valence band (VB). Some electrons transfer to the conduction band (CB) and get trapped by shallow (T1) and deep (T2) trap levels. Other electrons are excited to the 5d level and return to the ground state. Upon heat or near-infrared light stimulation, the trapped electrons escape from the traps, transition from the 5d level to the 4f level, and emit green fluorescence, indicating information readout.

3.3. Applications to OIS

As shown in Fig. 10(a), we built a simple experimental scheme for information writing and reading to demonstrate the application in optical storage. The optical information “N” was recorded on GAGG:Ce\(^{3+}\), Yb\(^{3+}\) ceramics with a 254 nm lamp under the cover of a photomask, and the information was read out by heating and optical stimulation. As shown in Figs. 10(b) and 10(d), the irradiated samples show green “N” when heated to 300°C and irradiated using 650 nm laser, respectively. Figures 10(c) and 10(e) represent that the sample with information is continuously irradiated or heated for 1 min, and the sample no longer emits light, indicating that the information has been erased.
ties ensure that GAGG:Ce3⁺ emission can be effectively written using a 254 nm Hg lamp and read the development of OIS materials.

Fig. 10. (a) Schematic illustration of the information storage and readout in ceramics; (b) and (c) the sample, with written information, is stimulated by 650 nm light and continuously stimulated for 1 min [with a filter]; (d) and (e) the sample with written information is heated to 300°C and held at 300°C for 1 min.

4. Conclusions

In summary, we have successfully developed an OIS medium, GAGG fluorescent ceramic, and greatly improved the trap density by co-doping Ce³⁺ and Yb³⁺ and a two-step sintering method. The properties of the trap levels have been investigated by TL curves, XPS, and EPR, and we have proposed the mechanism of optical storage of GAGG:Ce³⁺, Yb³⁺. Optical information can be effectively written using a 254 nm Hg lamp and read out through both heating and optical stimulation. These properties ensure that GAGG:Ce³⁺, Yb³⁺ is well suited as an optical storage medium, and this work is expected to contribute to the development of OIS materials.

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References


