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$Y_3Al_5O_{12}:Ce^{3+}$ fluorescent ceramic for optical data storage

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A kind of optical data storage medium based on electron-trapping materials, $Y_3Al_5O_{12}:Ce^{3+}$ fluorescent ceramic, was developed by vacuum sintering technology. The medium shows sufficiently deep traps (1.67 and 0.77 eV). The properties of trap levels were researched by thermoluminescence curves, and the optical storage mechanism based on Ce^{3+} ion doping was proposed. More importantly, the data can be written-in by 254 nm UV light, and readout by heating (300°C). This work expands the application fields of fluorescent ceramics, and it is expected to promote the development of electron-trapping materials.

Keywords: electron-trapping materials; optical data storage; $Y_3Al_5O_{12}$; Ce^{3+} doping.

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1. Introduction

The traditional optical data storage (ODS) materials are mainly azo metal chelates, cyanine dyes, and other organic dyes[1,2], which face considerable challenges due to poor physicochemical stability and low storage capacity. Therefore, it is of great significance to develop new optical storage media to advance the ODS applications. Electron-trapping materials (ETMs) have attracted a great deal of attention in the field of ODS due to their unique advantages of excellent rewritablity, environmental friendliness, high stability, and low cost. They are a kind of luminescent materials with light storage ability and delayed photon emissions under thermal stimulation or photostimulation[3]. It has a great application prospect in information storage[4–7], emergency display[8] and *ex vivo* bio-imaging[9–11].

Trap depth is one of the most important properties of ETMs, which affects the stability of optical information storage. However, the trap depth of ETMs could not meet the requirements for long-term information storage in previous research work. Hu *et al.* developed a novel phosphor $Ba_2SiO_4:Eu^{2+}, Ho^{3+}$ for optical storage: information can be stored by UV light and readout by thermal stimulation, but the trap depth is shallow (0.86 eV)[12]. Li's group reported $SrAl_2O_4:Eu^{2+}, Dy^{3+}$ phosphor for information storage: the trap depth is 0.7 eV[13]. In addition, Liu's group fabricated organics films with $Y_2GeO_5:Pr^{3+}, Tb^{3+}$ phosphors for information storage and realized writing-in and reading-out points in submicrometers[14]. Some researchers mixed phosphor and glass powder to prepare phosphor-in-glass as a storage medium[7,15]. Due to the poor uniformity of the above materials, they are not suitable as optical storage media. Therefore, it is urgent to develop suitable ETMs.

Yttrium aluminum garnet ($Y_3Al_5O_{12}$) fluorescent ceramics have attracted great attention due to their outstanding optical, thermal, and mechanical properties, and the ordered crystal structure of $Y_3Al_5O_{12}$ enables that information to be read and written with high accuracy. However, there are few reports of $Y_3Al_5O_{12}$ fluorescent ceramics in the field of ODS, although it has been widely used in the area of laser materials[16–18] and LEDs[19,20].

In this work, we prepared a series of $Y_3Al_5O_{12}$ fluorescent ceramics as information storage media, and a large number of deep traps were introduced. The optical characterization of samples is systematically studied by photoluminescence (PL), photoluminescence excitation (PLE), and thermoluminescence (TL) curves. We explained the optical storage mechanism based on Ce^{3+} ion doping. Finally, we demonstrated the optical information can be effectively written by a 254 nm Hg lamp, and readout by thermal stimulation. We believe that this research will further facilitate the development of advanced information storage technology.

2. Experiments

2.1. Preparation of ceramics

$Y_{3-x}Al_5O_{12}:x$Ce ($x = 0.011$, 0.013, 0.015, and 0.017) (abbreviated as YAG:xCe) were prepared by high temperature solid-state reaction. Chemical regents include Y_2O_3 (4N), Al_2O_3 (4N),

CeO_2 (4N), MgO, and tetraethyl orthosilicates (TEOs). MgO and TEOs act as the sintering aids in the process of ceramics preparation, and they can promote the reaction densification, as shown in Fig. 1. First, raw materials were mixed with anhydrous alcohol according to stoichiometric ratio [Fig. 1(a)] 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 [Fig. 1(b)]. 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 [Fig. 1(c)]. Then, the green bodies were presintered at 600°C for 3 h and further sintered at 1600°C for 6 h under vacuum conditions [Fig. 1(d)]. Finally, the YAG:Ce were double-surface-polished for characterizations.

2.2. Material characterization

X-ray diffraction (XRD) patterns of samples were measured by using an X-ray diffractometer (Bruker D8 ADVANCE) with CuKα radiation in the range of $2\theta = 10°$–$90°$. The scanning interval is 0.02°, and PL and PLE spectra were recorded by a Hitachi F-4600 fluorescence spectrophotometer with a 150 W xenon arc lamp as the light source. TL curves were measured by an SL08 TL meter (Radiation Science and Technology Co., Ltd, Guangzhou, China), using a high-pressure mercury lamp (254 nm) as the excitation source and with a photomultiplier tube detector (PMT; CR105, Beijing Hamamatsu, China). After being irradiated by a 254 nm Hg lamp for 5 min and waiting for 5 min, the sample was heated to 673 K, and the TL intensity was recorded.

3. Results and Analysis

3.1. Structure and optical properties

Figure 2 shows the XRD patterns of the $Y_{3-x}Al_5O_{12}$:xCe ($x = 0.011$, 0.013, 0.015, and 0.017) fluorescent ceramic; the diffraction peaks are well matched with the standard XRD pattern of $Y_3Al_5O_{12}$ (No. 33-0040), and no obvious impurity peaks are observed. This indicates that the Ce^{3+} does not change the structure of the matrix material.

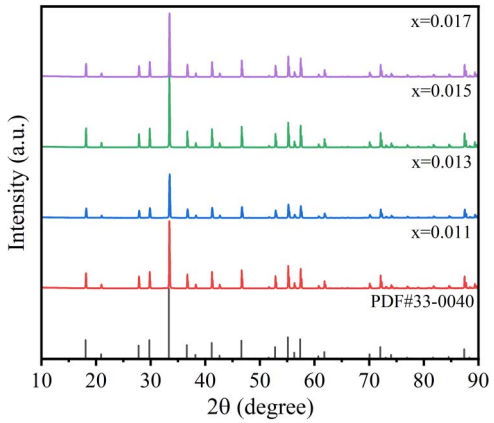


Fig. 2. XRD patterns of YAG:xCe ($x = 0.011$, 0.013, 0.015, and 0.017) and $Y_3Al_5O_{12}$ (PDF#33-0040).

As shown in Fig. 3(a), we tested the PLE spectrum (monitor wavelength: $\lambda_{em} = 540$ nm) and PL emission spectrum (excitation wavelength: $\lambda_{ex} = 450$ nm) of the YAG:xCe^{3+}. The excitation spectra have two broad bands located at 300–370 nm and 400–500 nm. These excitation peaks correspond to the 4f → 5d transition of Ce^{3+}. The emission peak under excitation of 450 nm of YAG:Ce^{3+} is located at 540 nm, showing a typical green luminescence that corresponds to the transitions of $5d_1 \rightarrow {}^2F_{5/2}$ and $5d_1 \rightarrow {}^2F_{7/2}$. When the 5d state electron transits to the ${}^2F_{5/2}$ and ${}^2F_{7/2}$, the two emission spectra superimpose an asymmetric broadband[21,22]. The spectral intensity of PL and PLE decreases with the increase of Ce^{3+} concentration, but the range of change is small.

Trap levels are closely related to the information storage properties of ETMs. They are generally analyzed by the TL curve. TL involves the process in which storage optical information by irradiation with light is re-emitted by heating. As an effective tool to study the trap levels, the TL spectrum provides much information about the depth and amount of trap levels. Trap depth is one of the most important properties of ETMs; it is closely related to the stability of long-term storage of information. Therefore, we tested the TL spectra of the YAG:xCe^{3+} ($x = 0.011$, 0.013, 0.015, and 0.017) at a heating rate of 1 K/s. Before the test, the sample was irradiated by 254 nm UV lamp for 300 s. Then we waited for 300 s to eliminate the afterglow.

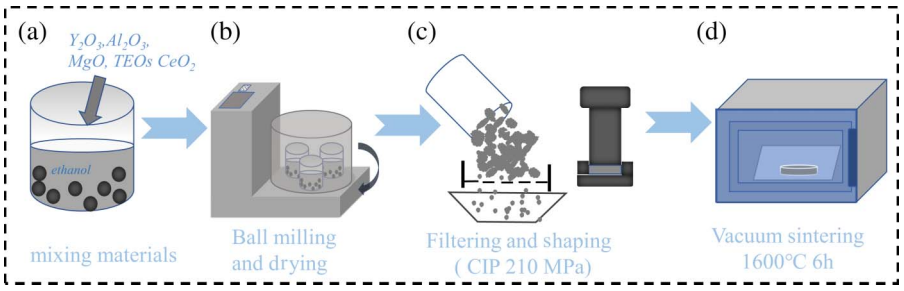


Fig. 1. Preparation flow chart of fluorescent ceramics. (a) Mixing and (b) ball milling and drying of raw materials, (c) filtering and shaping of samples, and (d) vacuum sintering of ceramics.

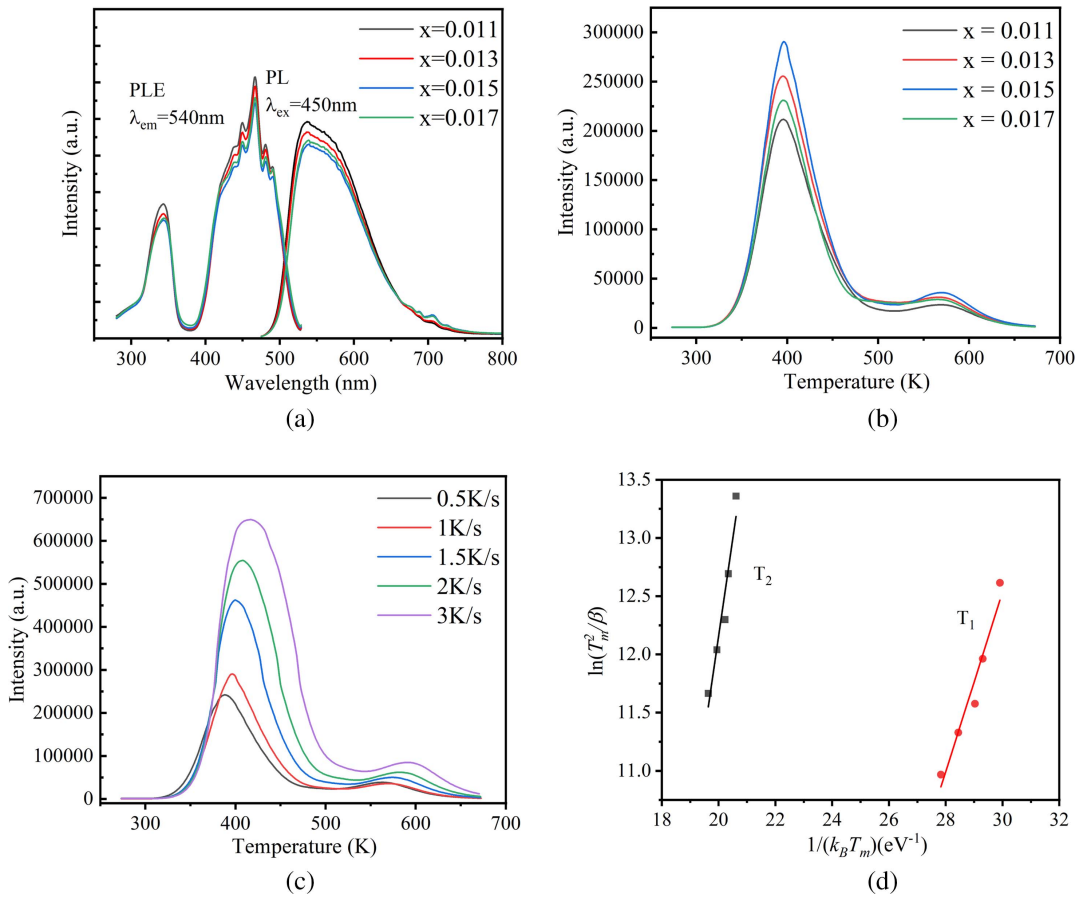


Fig. 3. (a) PLE and PL spectra of YAG:*x*Ce (x = 0.011, 0.013, 0.015, and 0.017); (b) TL curves of YAG:*x*Ce^{3+}; (c) TL curves with different heating rates of YAG:0.015Ce^{3+}; (d) ln(T_m^2/β) versus 1/(k_BT_m) based on Eq. (1), originating from two peaks (T_1 and T_2) at TL curve of YAG:0.015Ce^{3+}.

Finally, the sample was heated to 673 K and we recorded the TL intensity in the process. As shown in Fig. 3(b), the intensity of TL increases first and then decreases with the increase of Ce^{3+} concentration. When $x = 0.015$, the TL intensity reaches the maximum, and the concentration of Ce^{3+} ion was optimized at 0.015. In addition, with the increase of Ce^{3+} concentration, the intensity change of the emission spectrum is opposite that of the TL curves. This is because the excited electrons will be trapped by traps when the sample is irradiated by light, and as the number of carriers decreases, the emission intensity will decrease[23].

There are two TL peaks in YAG:Ce^{3+}, meaning that the sample contains two traps of different depths (T_1 and T_2). We used the Hoogenstraaten method to calculate the trap depth of YAG:0.015Ce^{3+}. First, a series of TL curves with different heating rates were measured, as shown in Fig. 3(c). The trap depths can be evaluated as the following [Eq. (1)][24,25]:

$$\beta E/k_B T_m^2 = s \exp\left(-E/k_B T_m\right), \tag{1}$$

where E (eV) is the trap depth; β (K/s) is the heating rate; k_B is the Boltzmann constant; T_m (K) is the peak temperature of the TL spectrum, and s (s^{-1}) is the frequency factor. By plotting ln(T_m^2/β) against 1/(k_BT_m), the depth of the trap for the TL curve can be determined according to the slope of a straight line, as shown in Fig. 3(d). The trap depths by fitting of YAG:0.015Ce^{3+} are 1.67 and 0.77 eV, which are larger than those of most typical ETM materials[26]. The sample was previously written by 254 nm UV light. After 30 min, the intensity of the TL peak of shallow traps decreased more obviously, which indicates that the electrons in the deep traps are stabler. This

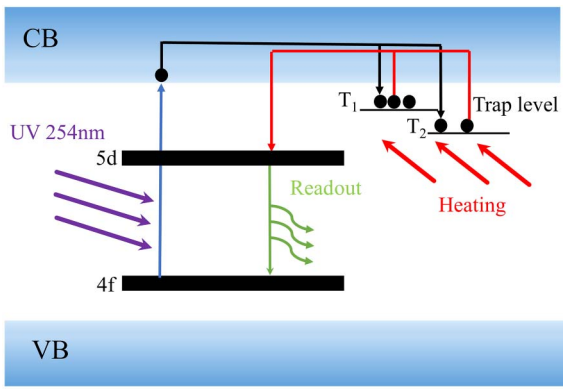
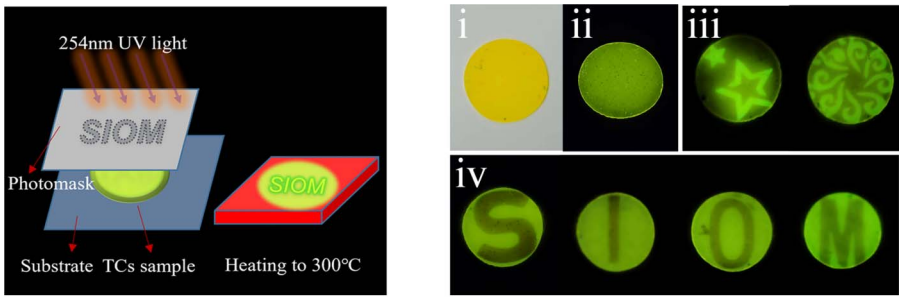


Fig. 4. Schematic of the optical storage mechanism of YAG:Ce.



(a) (b)

Fig. 5. (a) Schematic illustration of the information storage and readout in ceramics; (b) photographs of YAG:Ce^{3+} ceramics under (i) natural light; (ii) 254 nm Hg UV light; (iii) and (iv) under 254 nm UV light for 5 min and heated to 300°C showing stars, flower, "S", "I", "O" and "M", with photomask covering the sample.

provides the precondition for long-term stable storage of optical information.

3.2. Analysis of optical storage mechanism

We proposed the optical storage mechanism of the YAG:Ce, as shown in Fig. 4. In YAG:Ce, Ce^{3+} is not only the luminescence center, but also the electron donor. Under 254 nm light excitation (write-in), electrons are excited to 5d energy level from the ground state and generate holes in the VB. Some electrons can transfer to the conduction band (CB) and captured by trap levels (T_1 and T_2); others can only be excited to 5d energy level and returned to the ground state. The electrons in deep traps can exist for long time[27–29]. Under the stimulation of heating, electrons will escape from the traps and transition from the 5d to 4f energy level. This process will emit green fluorescence, indicating that the information is read out.

3.3. Applications to ODS

As shown in Fig. 5(a), we have established a simple experimental scheme of ODS and readout to demonstrate the application in ODS. Under the cover of the photomask, the optical information "SIOM" is recorded in YAG:Ce ceramics by 254 nm Hg lamp and the information is readout by heating. Figure 5(b) panel (i) was taken under natural light. When exposed to 254 nm light, a green PL is produced from YAG:Ce [Fig. 5(b) panel (ii)]; it corresponds to the 5d-4f transition of Ce^{3+}. As shown in Fig. 5(b) panel (iii), the irradiated sample shows a green flower and stars when heated to 300°C. Figure 5(b) panel (iv) shows the sample was covered by a mask and exposed to 254 nm UV light for 5 min, after heating to 300°C. The information of "S,""I," "O," and "M" was displayed.

4. Conclusions

In summary, we synthesized a series of fluorescent ceramics $Y_{3-x}Al_5O_{12}$:xCe^{3+} ($x = 0.011$, 0.013, 0.015, and 0.017) based on ETMs for optical information storage that exhibited deep trap levels (1.67 and 0.77 eV). The properties of trap levels were researched by TL curves, and we proposed an optical storage mechanism of YAG:Ce. Furthermore, optical information can be effectively written by 254 nm UV light, and read out by thermal stimulation. These features ensure that YAG:Ce is well suited to be an optical storage medium, and it is expected to provide candidate material for the next-generation ODS technology.

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