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2010 Chinese Phys. Lett. 27 047203

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Long-Lasting Phosphorescence Properties of Pyrochlore $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ Phosphor *CHU Ming-Hui(褚明辉)^{1,2}, JIANG Da-Peng(蒋大鹏)^{1**}, ZHAO Cheng-Jiu(赵成久)¹, LI Bin(李斌)¹¹Key Laboratory of Excited State Processes, Changchun Institute of Optics Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033²Graduate School of the Chinese Academy of Sciences, Beijing 100049

(Received 5 January 2010)

The $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$, which emits red color luminescence upon UV light excitation, is prepared by the conventional high-temperature solid-state method and its luminescent properties are systematically investigated. X-ray diffraction, photoluminescence, afterglow emission spectra and long-lasting phosphorescence (LLP) decay curves are used to characterize this phosphor. After irradiation by a 290-nm UV light for 3 min, the Pr^{3+} -doped $\text{La}_2\text{Ti}_2\text{O}_7$ phosphor emits intense red emitting afterglow from the $^1D_2 \rightarrow ^3H_4$ transitions, and its afterglow can be seen with the naked eye in the dark clearly for more than 1 h after removal of the excitation source. The afterglow decay curve of the Pr^{3+} -doped $\text{La}_2\text{Ti}_2\text{O}_7$ phosphor contains a fast decay component and another slow decay one. The possible mechanism of this red light emitting LLP phosphor is also discussed based on the experimental results.

PACS: 72.20.Jv, 78.55.Hx, 78.60.Lc

DOI: 10.1088/0256-307X/27/4/047203

The stoichiometric formula of lanthanide titanate $\text{La}_2\text{Ti}_2\text{O}_7$ was reported in the early 1950s and belongs to the family of perovskite layered structure compounds in monoclinic symmetry with a space group $P2_1$ (No. 11). This compound shows interesting dielectric, piezoelectric and ferroelectric properties with characteristics of a high Curie temperature and coercive fields.^[1–3] Up to date, the pyrochlore $\text{La}_2\text{Ti}_2\text{O}_7$ has found numerous applications such as a host for fluorescence centers, high temperature pigments, catalysts, ionic/electronic conductors, etc.^[1–4] Among all the properties reported on $\text{La}_2\text{Ti}_2\text{O}_7$, its photoluminescence properties were also found to be interesting. When doped with trivalent praseodymium Pr^{3+} , the $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ phosphor exhibits intense luminescence mainly in the blue and in the red region of the spectrum.^[5–8] The blue emission is essentially due to the transition from $\text{Pr}^{3+} \ ^3P_0$ excited state, whereas, the red emission originates from the transition from the 1D_2 excited state.^[5] The ratio between the blue emission and the red emission is dependent on the doped level of Pr^{3+} .^[6] It was also reported that the introduction of Al^{3+} codoping into the $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ phosphor could greatly improve its excitation efficiency and consequently obtain a higher emission intensity.^[7]

LLPs are a special kind of luminescence process with the decay times extending to seconds, minutes, or even hours after stopping the excitation. The occurrence of LLP are generally believed to be decided by two prerequisites: (1) the presence of abundant defects able to trap and immobilize free carriers, (2) the depths and the density of the defect traps existing in the host lattice should have appropriate values.^[9–11] Due to the special energy storing properties of LLP materials, such an afterglow effect has been widely used in many application fields including safety indication, emergency lighting, road signs, billboards,

graphic arts, and interior decoration.^[9–14] The structure of $\text{La}_2\text{Ti}_2\text{O}_7$ is built up of layers by $(\text{Ti}_2\text{O}_7)_n^{6n-}$ distorted perovskite-like slabs running parallel to the $\{110\}$ plane, bounds to each other by interlayer La^{3+} ions.^[6,15] The layers contain two kinds of vacancies in which the La^{3+} ions are nine-coordinated, while other La^{3+} ions are situated in eight- or seven-coordinated environments. In such a special crystal structure, it is expected that there are an abundance of point defects within the lattice,^[7] which gives the possibility to obtain LLP when doped with an activator. However, there is still no report on the LLP properties of impurity doped $\text{La}_2\text{Ti}_2\text{O}_7$ materials. Hence, a more complete investigation of the luminescence properties (especially the LLP properties) of impurity doped $\text{La}_2\text{Ti}_2\text{O}_7$ materials is encouraging, and could provide much valuable information when tailoring the LLP properties of $\text{La}_2\text{Ti}_2\text{O}_7$ based phosphors as efficient afterglow materials. In this Letter, the $\text{La}_2\text{Ti}_2\text{O}_7$ phosphors activated by Pr^{3+} ions have been prepared by solid-state reaction, and the characterization and luminescent properties have also been investigated.

The powder samples of Pr^{3+} -activated $\text{La}_2\text{Ti}_2\text{O}_7$ were prepared by the conventional high-temperature solid-state technique. The starting materials used in the preparation of these phosphors were high-purity La_2O_3 (> 99.999%), TiO_2 (> 99.99%), and Pr_6O_{11} (> 99.999%). The Pr^{3+} dopant concentrations ranged from 0.05 to 10 mol% of La^{3+} ions in $\text{La}_2\text{Ti}_2\text{O}_7$. The stoichiometrical amounts of raw materials were weighed and mixed homogeneously in an agate mortar, then placed into a corundum crucible positioned in the middle of the box furnace. The mixture was slowly heated to 1450°C and kept for 6 h in air atmosphere, following by subsequent air-cooling to obtain the product. In this work, the specimens obtained appear white in color.

Crystal structure of all synthesized powder sam-

*Supported by the National Natural Science Foundations of China under Grant No 50872130.

**Corresponding author. Email: jdp863@ciomp.ac.cn

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ples were identified by MSAL-XD-2 x-ray powder diffractometer (XRD) (Cu $K\alpha$ radiation, 40 kV, 30 mA and a scanning speed $3.0^\circ(2\theta)/\text{min}$). The XRD patterns matched quite well with the standard JCPDS files No. 28-0517.

The excitation and emission spectra were measured using a HITACHI model F-4500 fluorescence spectrophotometer with a photomultiplier tube operating at 700 V, and a 150 W Xe lamp was used as the excitation source. The emission spectra were corrected for photomultiplier tube response. The excitation spectra were obtained by scanning wavelengths from 200 to 400 nm monitored at emission position, and the emission spectra were scanned from 420 to 800 nm. The slits were set to be 2.5 nm and 5 nm for measuring excitation and emission spectra, respectively, during the whole experiment. The scan speed in the photoluminescence spectra measurements was set as 240 nm/min. Suitable filters were used to correct for the base line shift due to any stray light. The afterglow emission spectra and afterglow intensity decay curve were measured with the same HITACHI F-4500 fluorescence spectrophotometer. The UV excitation light was switched off after the sample had been irradiated for 3 min. The afterglow emission spectra were recorded using the kinetic analysis mode. The scan speed of the afterglow emission spectra was increased to 3600 nm/min in order to ensure that the intensity change during the measurement is negligible.

Lifetime measurements were carried out using a Nd:YAG laser system (Spectra Physics). The obtained, unweighted, data were analyzed by the exponential fitting technique using the Origin 7.5 software. All the measurements for the as-synthesized samples were performed at room temperature.

The crystal structure of lanthanide titanate $\text{La}_2\text{Ti}_2\text{O}_7$ was reported as being built up by $(\text{Ti}_2\text{O}_7)_n^{6n-}$ distorted perovskite-like slabs running parallel to the $\{110\}$ plane, bounds to each other by interlayer La^{3+} ions.^[6,15] To make sure that our results are reliable, we carefully prepared our samples and the materials investigated were checked for the structural and phase purity. The representative XRD pattern of $\text{La}_2\text{Ti}_2\text{O}_7:1\%\text{Pr}^{3+}$ sample is shown in Fig. 1. It is obvious that our sample is chemically and structurally $\text{La}_2\text{Ti}_2\text{O}_7$ because the final obtained sample has no detectable amount of impurity and the XRD peak positions of the doped sample are similar to those of the JCPDS Card No. 28-0517. According to the ionic radius matching rule, the Pr^{3+} ions ($r_{\text{Pr}^{3+}} = 0.101 \text{ nm}$) are expected to occupy the La^{3+} sites ($r_{\text{La}^{3+}} = 0.106 \text{ nm}$) sites. According to the XRD analysis results, the introduction of Pr^{3+} is found without disturbing the $\text{La}_2\text{Ti}_2\text{O}_7$ crystal lattice. The Pr^{3+} ions are expected to be uniformly introduced into the $\text{La}_2\text{Ti}_2\text{O}_7$ crystal lattice because the praseodymium titanate ($\text{Pr}_2\text{Ti}_2\text{O}_7$) is isostructural to $\text{La}_2\text{Ti}_2\text{O}_7$.^[16]

A series of $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ phosphors have been

synthesized with various Pr^{3+} dopant levels. The emission spectrum of $\text{La}_2\text{Ti}_2\text{O}_7:1\%\text{Pr}^{3+}$ at room temperature is shown in Fig. 2. It is clear from this figure that typical Pr^{3+} emissions presumably induced by the excitation through the host are clearly observed. The emission spectra for $\text{La}_2\text{Ti}_2\text{O}_7:1\%\text{Pr}^{3+}$ phosphor exhibits the typically narrow-line features of rare-earth ions and consisted of two major groups in the blue and red spectral regions, which are attributed to the transitions from the 3P_0 and 1D_2 excited states to the ground state of Pr^{3+} , respectively.^[11] It can also be found that the emission lines of Pr^{3+} are broadened somewhat because there are several Stark levels for the excited and ground state levels of Pr^{3+} . The blue emission from $^3P_0 \rightarrow ^3H_4$ transition, corresponding to the emission line at 490 nm, is relatively weaker compared to the red 611 nm emission ($^1D_2 \rightarrow ^3H_4$) and comprises only about 1% of the total photoluminescence intensity, therefore, the strongest $^1D_2 \rightarrow ^3H_4$ transition makes the sample emission red. The lifetime of the strongest $^1D_2 \rightarrow ^3H_4$ transition was measured to be 2.1 ms using a Nd:YAG pulsed laser (266 nm). The excitation spectrum was recorded when the strongest 611 nm emission of Pr^{3+} was monitored and presented in Fig. 2. It is found that there is a broad band in the wavelength region 210–320 nm, in addition to a weaker band located at about 340 nm. The former excitation band with the wavelength shorter than 320 nm is involved in the interband transition of the $\text{La}_2\text{Ti}_2\text{O}_7$ host whose band gap is about 3.82 eV,^[3] and the latter shoulder band can be assigned to the $4f-5d$ transition of Pr^{3+} .^[5,11] The emission spectra obtained under host absorption band and $4f-5d$ transition band excitation don't show any difference except the intensity. The absence of any narrow peaks originated from $f-f$ transitions of Pr^{3+} indicates that the excitation energy is absorbed by the host lattice first and then transfer to the Pr^{3+} resulting in the narrow emissions of Pr^{3+} .

It is well known that in phosphor materials the photon emission intensity of RE activator ions exhibits an optimum concentration. It is difficult for the phosphor materials to create efficient emission when the RE activator ion concentration is too low. On the other hand, the cross-relaxation interaction between the nearest RE activator ions will quench the emission if the RE activator ions excess its optimum content. The dependence of the 611 nm red light emission and the 490 nm blue emission intensity ($\lambda_{ex} = 291 \text{ nm}$) on Pr^{3+} dopant concentration in $\text{La}_2\text{Ti}_2\text{O}_7$ phosphors is shown in Fig. 3. The experimental results reveal that the luminescence intensity of Pr^{3+} -doped $\text{La}_2\text{Ti}_2\text{O}_7$ increases with the Pr^{3+} dopant concentration. The 611 nm emission intensity reaches its maximum when the concentration of Pr^{3+} is up to about 0.3% and then diminishes markedly with increasing Pr^{3+} concentration. This behavior is due to the increased energy transfer between two neighboring Pr^{3+} with increasing quantity of Pr^{3+} , consequently

quench its emission. The 490 nm blue light emission in Pr^{3+} -doped $\text{La}_2\text{Ti}_2\text{O}_7$ slightly increases with the Pr^{3+} concentration and quenches the emission till or above about 5%. The different quenching behaviors between the red and blue emission in Pr^{3+} -doped $\text{La}_2\text{Ti}_2\text{O}_7$ can be explained by the fact that there are two categories of different La^{3+} site environments in the host lattice, which will be replaced by the Pr^{3+} ions. It is reported that the Pr^{3+} ions accommodated in the inter-layer space exhibit the red $^1D_2 \rightarrow ^3H_4$ luminescence, whereas the Pr^{3+} ions distributed inside the distorted perovskite-like layers are responsible for the 490 nm blue emission ($^3P_0 \rightarrow ^3H_4$).^[5]

The photoluminescence properties of the $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ phosphor has been reported.^[5–8] However, there is no report on the LLP properties of this phosphor up to now. A very important result of our present work is that we have observed obvious LLP emission in the above-mentioned Pr^{3+} -doped $\text{La}_2\text{Ti}_2\text{O}_7$ phosphor. The afterglow emission possesses the same quenching concentration as the photoluminescence as shown in Fig. 3. As shown in Fig. 4, we have measured the long-lasting afterglow emission spectra of $\text{La}_2\text{Ti}_2\text{O}_7:0.3\%\text{Pr}^{3+}$ sample at different times after switching off the 290 nm excitation source. The afterglow emission spectra were observed in the wavelength range as the same as the UV-excited emission spectra. Moreover, they are similar in shape and the peak positions compared to those of fluorescence spectra under 290 nm excitation, as shown in Fig. 2, indicating that the LLP of $\text{La}_2\text{Ti}_2\text{O}_7:0.3\%\text{Pr}^{3+}$ is due to the f - f transition of Pr^{3+} , that is to say, the radiating centers in both the cases are identical.

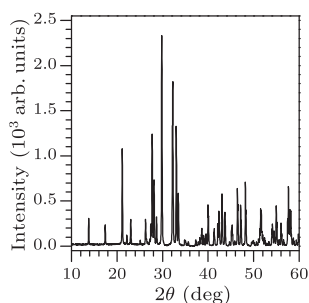


Fig. 1. XRD pattern of $\text{La}_2\text{Ti}_2\text{O}_7:1\%\text{Pr}^{3+}$ phosphor.

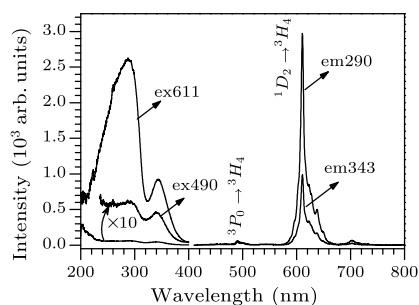


Fig. 2. Excitation and emission spectra of the 1% Pr^{3+} -doped $\text{La}_2\text{Ti}_2\text{O}_7$ phosphor.

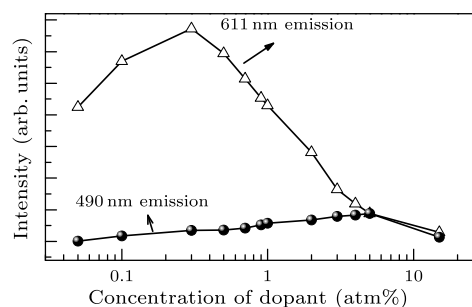


Fig. 3. Dependence of the 611 nm red light emission and the 490 nm blue emission intensity on Pr^{3+} dopant concentration in $\text{La}_2\text{Ti}_2\text{O}_7$ phosphors ($\lambda_{ex} = 290$ nm).

Theoretically speaking, LLP arises from the fact that charge carriers (i.e., electrons and/or holes) generated by the excitation are trapped at certain defect traps, and their detrapping is thermally activated at room temperature.^[11,17–19] Consequently, it is expected that the LLP phenomenon can be observed if there are adequate hole traps and electron traps with suitable depths in the host lattice.^[10]

The ionic radii of La^{3+} , Pr^{3+} , and Ti^{3+} ions are 1.06, 1.01 and 0.77 Å, respectively. Hence, it is unlikely that a significant number of Pr^{3+} ions occupy

The 490 nm blue emission of Pr^{3+} in $\text{La}_2\text{Ti}_2\text{O}_7$ only contributes about 1% and lasts too fast to be recorded by the F-4500 fluorescence spectrophotometer under the same experiment conditions, therefore, the LLP emission of this phosphor show as red light during the whole decay period.

Figure 5 shows that the afterglow intensity decay curve of $\text{La}_2\text{Ti}_2\text{O}_7:0.3\%\text{Pr}^{3+}$ phosphor monitoring at 611 nm after the 290-nm ultraviolet has been removed. The afterglow emission decreases quickly at first and then very slowly. The multi-exponential afterglow decay model of Pr^{3+} -doped $\text{La}_2\text{Ti}_2\text{O}_7$ phosphor is fully in line with the behavior of a wide variety of rare-earth-ion-doped LLP phosphors.^[9–11] In this model, the experimental data have been analyzed by curve fitting and it is found that these decay curves can be well fitted using the biexponential decay function as follows:^[11] $I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where I and I_0 are the phosphorescence intensities; A_1 and A_2 are constants; t is time; τ_1 and τ_2 are the decay times for the exponential components, respectively. The long-afterglow-decay fitting results are also given in Fig. 5. These parameters reveal that the decay processes of $\text{La}_2\text{Ti}_2\text{O}_7:0.3\%\text{Pr}^{3+}$ phosphor behaves in terms of a double-exponential decay model. At first it acts on the first exponential, then when the decay time is longer, the decay acts on the second exponential.^[9,11] Due to the second significant slow decay component, the phosphorescence of the Pr^{3+} -doped $\text{La}_2\text{Ti}_2\text{O}_7$ phosphors can be seen with the naked eyes (0.32 mcd/m²) in the darkroom for more than 1 h after the 290 nm UV irradiation source has been removed.

the $\text{Ti}^{3+}/\text{Ti}^{4+}$ ions sites in the host lattice since the difference between the radii of Pr^{3+} and Ti^{3+} are relatively large. Clearly, Pr^{3+} replaces La^{3+} in the regular cation site rather than squeezes into the interstitial position deforming strongly the lattice. Moreover, the isostructural character of $\text{Pr}_2\text{Ti}_2\text{O}_7$ compared to $\text{La}_2\text{Ti}_2\text{O}_7$ further provides the evidence that the Pr^{3+} ions will be well doped into the lattice sites to yield good solid solubility. It was reported that in the $\text{La}_2\text{Ti}_2\text{O}_7$ host lattice, the titanium ions will coexist as Ti^{3+} and Ti^{4+} .^[4] In this case, the charge

compensation will be performed by the La^{3+} vacancies. The formation of vacant La^{3+} sites should be rather expected during high temperature firing process, which is widely reported in other impurity doped LLP phosphor.^[9,11,19,20] The other way of the charge compensation is via creation of $\text{Pr}_{\text{La}\bullet}$ positive charge point defect during the synthesis process, which is also feasible because the oxidization of Pr^{3+} to Pr^{4+} is relatively easy.^[11] In this way, two Pr^{4+} replace three La^{3+} ions to balance the charge of these phosphors, which create two $\text{Pr}_{\text{La}\bullet}$ positive defects and one $V_{\text{La}''}$ negative defect.^[11] This process can be written as: $2\text{Pr}^{4+} + 3\text{La}^{3+} \rightarrow 2\text{Pr}_{\text{La}\bullet} + V_{\text{La}''}$.

The detailed description of LLP mechanism is not yet known. The LLP phenomenon is assumed to be due to the thermostimulated recombination of holes and electrons which leave electrons or holes in a metastable state at room temperature.^[9] After irradiation, excited electrons and holes are formed in the samples. The excited holes or electrons are trapped by different defect centers, released by heat at room temperature, and recombine with electrons or holes trapped by other defect centers. The released energy due to the recombination of holes and electrons is transferred to the rare earth ions, finally leads to the characteristic rare-earth ion emissions. In the Pr^{3+} -doped $\text{La}_2\text{Ti}_2\text{O}_7$ system, the vacancies $V_{\text{La}''}$ may be one of the hole-trapping centers, and the $\text{Pr}_{\text{La}\bullet}$ site impurity trap, formed by Pr^{4+} replace La^{3+} , may

serve as the electron trap. To confirm this assignment, $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ codoped with LaF_3 has also been synthesized. The results reveal that the addition of 1% LaF_3 can greatly reduce the LLP performance, indicating that the addition of F^- ions has significantly reduced the positive $\text{Pr}_{\text{La}\bullet}$ defects density.

Based on the above-mentioned results and the previous reported mechanism by Hosono *et al.*^[21–23] on the persistent luminescence of photo-oxidizable impurities-doped phosphors, the processes of $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ LLP phosphor can be simply treated and illustrated in Fig. 6. With UV irradiation, the photo-oxidized reaction of Pr^{3+} ions in $\text{La}_2\text{Ti}_2\text{O}_7$ would occur to generate $(\text{Pr}^{3+})^+$ and the excited electrons e^* . Then e^* would be trapped on the electron traps. By this way, $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ would be able to store the energy of excitation light during UV irradiation. After turning off the excited source, the trapped e^* would be thermally excited and released from the electron-traps by thermal energy at room temperature because the energy level of the electron-traps are relatively low. The released e^* would recombine with $(\text{Pr}^{3+})^+$ to produce the excited state of Pr^{3+} ions. Finally, result in the red phosphorescence due to the $^1D_2 \rightarrow ^3H_4$ transition. Because the release ratio of the trapped electrons releasing from the electron traps is properly slow near room temperature, the red-light-emitting LLP of Pr^{3+} in $\text{La}_2\text{Ti}_2\text{O}_7$ can last for about one hour.

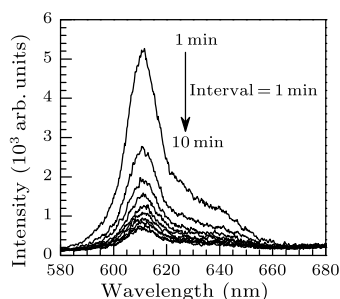


Fig. 4. Afterglow emission spectra of $\text{La}_2\text{Ti}_2\text{O}_7:0.3\%\text{Pr}^{3+}$ phosphor at different times after removal of the excitation source.

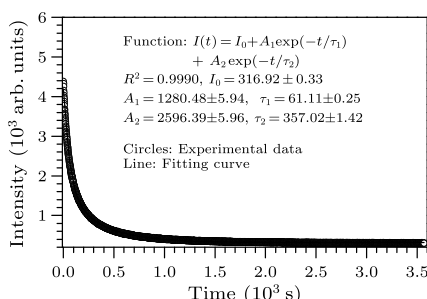


Fig. 5. Afterglow emission decay curve of $\text{La}_2\text{Ti}_2\text{O}_7:0.3\%\text{Pr}^{3+}$ phosphor monitoring at 611 nm. Sample was irradiated by 290-nm light for 3 min before measurement.

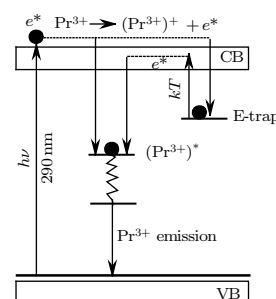


Fig. 6. Possible processes for the origin of the LLP in $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ phosphor.

In summary, a novel rare-earth titanate long-lasting phosphor $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ has been reported. The photoluminescence results reveal that the strongest $^1D_2 \rightarrow ^3H_4$ transition of Pr^{3+} makes the $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ emit red light. Furthermore, the $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ phosphor shows an extraordinary afterglow emission, being maintained for a time exceeding 1 h after removal of the excitation source.

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