

Synthesis and Luminescent Properties of a New Yellowish-Orange Afterglow Phosphor $Y_2O_2S:Ti,Mg$

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Luminescence that persists after the removal of the excitation is called afterglow or persistent phosphorescence. Material with the afterglow property can be used in many fields, including traffic signs, interior decoration, and light sources. The first record of persistent phosphorescent material is in the Song dynasty of China (11th century A.D.).¹ In the miscellaneous notes by a Song monk, of which the title is Xiang-Shan Ye-Lu, there is a story about a long lasting phosphorescent painting. On the painting was a cow that appeared during the daytime as eating grass outside the pen, but at night as resting in it. The ink that was shown in the dark for a given duration after absorption of light is long lasting phosphorescent material.

In the 18th century, people in Europe synthesized afterglow phosphors by using sea shells and sulfur.² In the beginning of the 20th century, the ZnS:Cu phosphor has been known as a long phosphorescent phosphor and used in a variety of applications. This phosphor shows green emissions peaking at 530 nm, which suits the visual perception of the human eye very well. However, it is not bright enough for many applications and does not maintain its phosphorescence for more than a few hours. Therefore, to sustain phosphorescence, radioactive elements, such as radium (⁸⁸Ra), tritium (³H), and promethium (¹⁴⁷Pm), were added to ZnS:Cu phosphor. Such paints have been used for luminous watches and clocks. However, for safety and environmental considerations, there is a serious demand for the development of a radioactive-free long phosphorescent phosphor at the present time.

In the 1960s and early 1970s, the SrAl₂O₄:Eu²⁺ phosphor has been known to be a green phosphor with an emission peak at 520 nm due to 4f⁶5d to 4f⁷ transition of europium ion (Eu²⁺), and this phosphor is mainly for

fluorescent lamp and cathode ray tube (CRT) applications.^{3–6} In 1995, Matsuzawa et al.^{7,8} successfully synthesized a Eu²⁺ and dysprosium ions (Dy³⁺) coactivated SrAl₂O₄ phosphor. After excitation by the UV light, it exhibits greater brightness, longer persistent green phosphorescence, and better chemical stability than that of the ZnS:Cu phosphor. Matsuzawa et al.⁷ suggested a mechanism for the afterglow phenomenon. Dy³⁺ ion serves as a trap center, and long lasting phosphorescence is caused by the trapping and thermal release of holes at Dy³⁺ ions in the system.

Europium ion-doped Y₂O₂S red-emitting phosphor has been used in the field of CMT (color monitor tube) and high-resolution CRTs (cathode ray tubes) because of the higher efficiency compared with europium-doped Y₂O₃ phosphor. However, until now, yellowish-orange afterglow phosphor with Y₂O₂S compound as a host lattice structure has not been reported. In this study, a new yellowish-orange afterglow phosphor Y₂O₂S:Ti,Mg was synthesized. Its luminescent properties and mechanism were investigated.

(Y_{2-x-y}Ti_xMg_y)O₂S (x = y = 0.01) phosphor was synthesized by solid-state reaction with Y₂O₃, S, TiO₂, and MgO as raw materials. Sodium carbonate (Na₂CO₃) was added as a flux. The molar ratio of Y:Ti:Mg:S is 1.98:0.01:0.01:6, respectively. Stoichiometric mixtures of highly pure raw materials were homogeneously mixed and sintered at high-temperature ranging from 900 to 1200 °C for 2–3 h under nitrogen gas. After the firing process, powders were washed with water to remove the residual flux and flux byproduct. Then, the product was washed with 0.5 M HNO₃ solution for a clean and smooth particle surface.

The crystal structure and phase of the synthesized samples were analyzed by X-ray powder diffraction (XRD) with a wavelength of Cu Kα. The structure was refined with the program GSAS.⁹ The peak shape was modeled with a pseudo-Voigt function. The fwhm (full width at half-maximum) was refined as a function of 2θ, taking into account both Gaussian and Lorentzian broadening. The background was modeled as a 12-term polynomial function. Cell parameters, scale factor, and the background polynomial functions were free variables during refinements. The luminescence properties and afterglow phenomenon were studied by a SPEX Fluorolog-2 spectrometer. The excitation source was a Xe lamp. All measurements were carried out at room temperature.

Figure 1 shows the comparison between the observed and calculated patterns as well as the difference curve

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Table 1. Crystallographic Data of the $(Y_{2-x-y}Ti_xMg_y)O_2S$ ($x = y = 0.01$) Phosphor^a

atoms	x	y	z	U_{iso} (\AA^2) $\times 100$	occupancy
Y	0.666667	0.333333	0.28203(12)	1.863(18)	0.9800
Ti	0.666667	0.333333	0.28203(12)	1.863(18)	0.0100
Mg	0.666667	0.333333	0.28203(12)	1.863(18)	0.0100
S	0.000000	0.000000	0.000000	1.95(7)	1.0000
O	0.666667	0.333333	0.6285(5)	2.09(13)	1.0000

space group	cell parameters	reliability factors	bond angle (deg)	interatomic distances (\AA)
$P\bar{3}M1$	$a = b = 3.78524(8) \text{\AA}$ $c = 6.58809(14) \text{\AA}$	$R_p = 7.03\%$ $R_{wp} = 10.41\%$ $\chi^2 = 1.69$	O–M–O $\times 3$ 74.90(9) O–M–O $\times 3$ 113.47(3) S–M–S $\times 1$ 82.567(18) S–M–O $\times 6$ 78.52(7) S–M–O $\times 3$ 130.372(12) S–M–O $\times 3$ 154.73(10)	M–O $\times 3$ 2.2635(10) M–O $\times 1$ 2.282(4) M–S $\times 3$ 2.8685(5)

^a M = Y, Ti, and Mg.

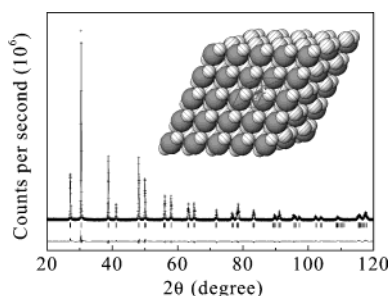


Figure 1. Rietveld fits to powder XRD data for $(Y_{2-x-y}Ti_xMg_y)O_2S$ ($x = y = 0.01$). Experimental (crosses), theoretical (solid line), reflection positions (vertical bars), and difference between observed and calculated intensity (solid line at the bottom). Upper right, structure of Y_2O_2S . Yttrium (small balls), oxygen (medium balls), and sulfur (big balls).

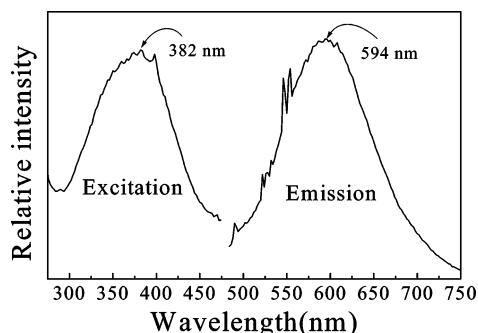


Figure 2. Emission and excitation spectra of the $(Y_{2-x-y}Ti_xMg_y)O_2S$ ($x = y = 0.01$) phosphor.

of the $(Y_{2-x-y}Ti_xMg_y)O_2S$ ($x = y = 0.01$) powder. The factors of the refinement are $R_p = 7.03\%$, $R_{wp} = 10.41\%$, and $\chi^2 = 1.69$, respectively. Judging from the XRD patterns and the refinement data, the $(Y_{2-x-y}Ti_xMg_y)O_2S$ ($x = y = 0.01$) phosphor has a hexagonal structure with the lattice constants of $a = b = 3.78524(8) \text{\AA}$ and $c = 6.58809(14) \text{\AA}$. The upper right part of Figure 1 is the corresponding structure of $(Y_{2-x-y}Ti_xMg_y)O_2S$ ($x = y = 0.01$). Ti and Mg ions randomly substitute the position of yttrium in the Y_2O_2S compound. The atomic parameters derived from the refinements are given in Table 1.

Figure 2 shows excitation and emission spectra of the $(Y_{2-x-y}Ti_xMg_y)O_2S$ ($x = y = 0.01$) phosphor. The excitation maximum appears at 382 nm and emits luminescence with a peak wavelength of 594 nm. The broad peaks of spectra indicate that the excitation and emission processes are caused by charge transfer transition. Figure 3 is the corresponding CIE chromaticity graph.

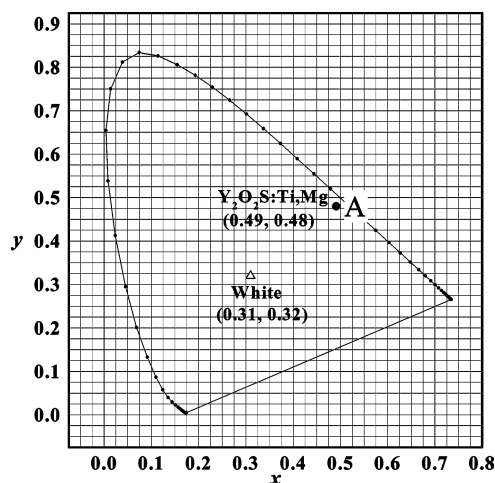


Figure 3. Chromaticity of the $(Y_{2-x-y}Ti_xMg_y)O_2S$ ($x = y = 0.01$) phosphor.

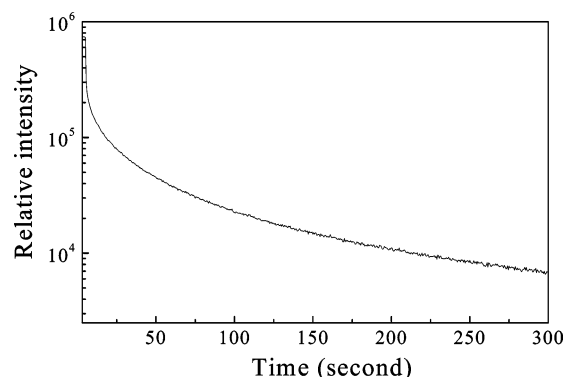


Figure 4. Persistent phosphorescence characteristics of $(Y_{2-x-y}Ti_xMg_y)O_2S$ ($x = y = 0.01$) phosphor measured at 24 °C after removal of the excitation source.

Point A with chromaticity coordination of (0.49, 0.48) in Figure 3 locates in the region of yellowish-orange color. Afterglow characteristics, after the removal of light excitation, are shown in Figure 4. It is obvious that the incorporation of the Ti and Mg ions gives rise to the $(Y_{2-x-y}Ti_xMg_y)O_2S$ phosphor with a yellowish-orange afterglow effect.

It was suggested that the persistence of phosphorescence and long decay time of $SrAl_2O_4:Eu,Dy$ phosphor are due to the trapping mechanism resulting from Dy^{3+} ions doping.⁷ Much research has been done to investigate the principle of the afterglow phenomenon.^{10–18} Single crystals, fibers, polycrystals, and thin films of the

SrAl₂O₄:Eu,Dy phosphor were synthesized for studying. Furthermore, photocurrent measurements, thermal luminescence, and theoretical calculations were adopted to investigate the mechanism of phosphorescent dynamics. Here, we propose that introduction of the Ti and

Mg ions to the Y₂O₂S compound causes the formation of new electronic donating and accepting levels between the host lattice band gap. One of the two kinds of ions absorb energy and thermally transfer the excited electrons to the other kinds of ions which serve as trap centers. The trapping of excited electrons and thermally released processes caused the appearance of afterglow. A detailed study of the mechanism is underway.

In summary, a new yellowish-orange afterglow phosphor (Y_{2-x-y}Ti_xMg_y)O₂S was synthesized by solid-state reaction under a nitrogen atmosphere. The introduction of Ti and Mg ions produced complex trap centers and resulted in the afterglow phenomenon.

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