

Optical and ESR studies of persistent phosphor Ce^{3+} -doped CaYAl_3O_7

Mitsuo Yamaga^{a,*}, Yusuke Ohsumi^a and Nobuhiro Kodama^b

^aDepartment of Mathematical and Design Engineering, Gifu University, Gifu 501-1193, Japan

^bDepartment of Materials Science and Engineering, Akita University, Akita 010-8502, Japan

Fluorescence from CaYAl_3O_7 (CYAM) melilite crystal doped with Ce^{3+} excited at 266 or 355 nm has a broad band with a peak at 430 nm. The decay time of the Ce^{3+} fluorescence is 45 ns below 300 K. Persistent phosphorescence, of which the line shape is the same as that of the Ce^{3+} fluorescence, has fairly long decay times distributed in the range from 1 to 1000 s. After irradiating CYAM:Ce with the UV light at 300 K, ESR spectra measured at 77 K consist of a single resonance line with a g value of 2.002 and two sets of the sextet-hyperfine lines with a g value of 2.012 due to the hyperfine coupling with Al nuclear spin ($I = 5/2$). The g values of these ESR lines indicate that an electron is trapped at an oxygen vacancy and a hole is self-trapped around a single Al^{3+} ion. We have proposed a mechanism responsible for the persistent phosphorescence in CYAM:Ce, taking into account the crystal structure and the ESR results.

Key words: Persistent phosphorescence, Electron-spin resonance, Photoconductivity, Cerium ions, Melilite crystal.

Introduction

Ce^{3+} -doped materials are attractive for applications such as lasers, scintillators, and phosphors [1]. Ce^{3+} -doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG:Ce) crystals were applied to an orange phosphor used for a white LED [2, 3]. However, deficits created in the garnet crystals during the crystal growth process decreased the quantum yield of the Ce^{3+} fluorescence. Recently, persistent afterglow associated with oxygen deficits in $\text{Y}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$ (YSGG) was observed [4]. The excitation energy was stored in the form of trapped electrons and holes [4, 5].

In a previous paper [6], we reported properties of persistent phosphorescence from $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (CASM) melilite crystals doped with Ce^{3+} and proposed a mechanism responsible for the persistent phosphorescence. CaYAl_3O_7 (CYAM) belongs to the same melilite family and is represented by the space group D_{2d}^3 as shown in Fig. 1 [7]. Ca^{2+} and Y^{3+} ions, being sandwiched between two pentagonal rings composed of five AlO_4 tetrahedra, are eightfold-coordinated and randomly distributed in the lattice keeping a composition ratio of 1:1. The melilite crystal has layer structure connecting the pentagonal rings with each other in the c plane [6, 7]. Such layer structure plays an important role in formation and migration of holes, for example, in CASM:Ce [6] and Eu^{2+} -doped SrAl_2O_4 (SAO:Eu) [8].

In this paper, we report on the optical and electron-spin resonance (ESR) spectroscopy of Ce^{3+} -doped CaYAl_3O_7 (CYAM:Ce). Taking into account the

relation between the crystal structure and the optical, photoconductivity and ESR results, we propose a mechanism responsible for the persistent phosphorescence in CYAM:Ce.

Experimental Procedure

CYAM:Ce single crystals were grown using the high-temperature Czochralski technique [6]. The cerium concentration was 0.1 mol % at the starting charge.

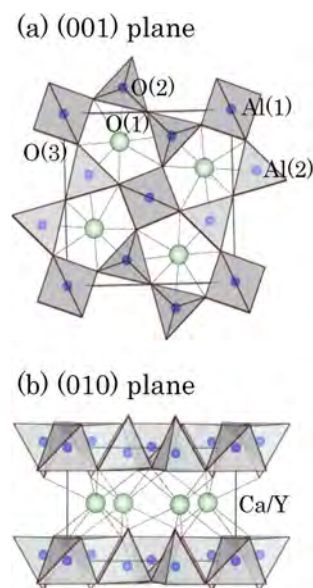


Fig. 1. The projections of the melilite crystal structure of CaYAl_3O_7 (CYAM) in (a) the (001) plane and (b) the (010) plane. [O(1), O(2), O(3)] and [Al(1), Al(2)] denote lattice sites of oxygen and aluminum. Ca^{2+} and Y^{3+} are eightfold coordinated and randomly distributed in the lattice keeping a composition ratio of 1:1.

*Corresponding author:
Tel : +81-58-293-3052
Fax: +81-58-293-2415
E-mail: yamaga@gifu-u.ac.jp

Optical absorption, fluorescence and excitation spectra were measured in the temperature range between 10 and 300 K using the tunable source (100–600 nm) in the UVSOR facility at Institute for Molecular Science. Fluorescence decay curves were measured using the third or fourth harmonics (355 or 266 nm) output from a Spectra-Physics GCR100 pulsed Nd:YAG laser with a pulse width of 10 ns and a Hamamatsu Photonics R943-02 PMT detector, connected to a Yokogawa DL1740 digital oscilloscope and a personal computer (PC). Persistent phosphorescence was measured after a sample was irradiated with the ultraviolet (UV) light of 355 or 266 nm for five minutes. Optical signals after removal of the UV light were sampled at 10 kHz, integrated over a period of 1 second, and passed through an A to D converter connected to a PC. Sample temperatures between 20 and 300 K or between 77 and 500 K were achieved using an Iwatani CA201 cryo-refrigerator or an Oxford OptistatDN-V, respectively.

Thermoluminescence (TL) measurements [5] were the same as the persistent phosphorescence measurements except that intensities were detected as a function of temperature at a heating rate of 0.2 K s^{-1} .

Photocurrents under irradiation of the UV light were measured at 300 K using an Advantest R8240 digital electrometer synchronized by a trigger from a Nd-YAG pulsed laser when a DC voltage was applied to electrodes attached on the surface of the sample and varied from 0 to 50 V.

After irradiating the sample with the UV light at 300 K, ESR measurements were carried out using a JES-FA100 X-band spectrometer with ~ 9.06 or ~ 9.16 GHz when measured at 77 or in the range from 100 to 300 K, respectively. The temperature of 77 K was obtained by immersing the sample into a liquid nitrogen dewar. The temperature in the range from 100 to 300 K was obtained by spraying the sample with temperature-controlled nitrogen gas evaporating from liquid nitrogen.

Results

Optical spectra

Figure 2 shows the absorption, fluorescence and excitation spectra of CYAM:Ce when measured at 10 K. The absorption spectrum of CYAM:Ce consists of unresolved broad bands in the range of 100–400 nm. The blue fluorescence excited at 200 nm has a broad band with a peak at 430 nm, denoted by D. The two optical transitions from the energy level of the $^2E(5d)$ lowest excited state of Ce^{3+} to the low lying $^2F_{5/2}(4f)$ and $^2F_{7/2}(4f)$ ground states with the energy separation of about 2000 cm^{-1} could not be resolved because of inhomogeneous broadening created by random distribution of Ca^{2+} and Y^{3+} ions in the CYAM crystal [6]. The excitation spectrum obtained by monitoring the fluorescence intensity at 430 nm is different from the absorption spectrum. The broad bands denoted by A

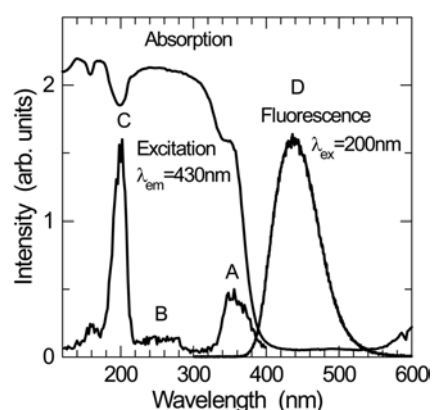


Fig. 2. Absorption, fluorescence and excitation spectra observed in CYAM:Ce at 10 K.

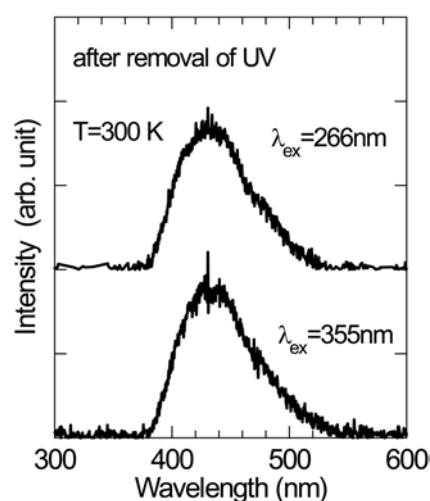


Fig. 3. Persistent phosphorescence spectra observed in CYAM:Ce after removal of 266 nm or 355 nm light at 300 K.

and B are assigned to the five optical transitions from the $^2F_{5/2}(4f)$ ground state of Ce^{3+} to the $^2E(5d)$ and $^2T_2(5d)$ excited states, respectively [2, 6, 9]. The intense band around 200 nm denoted by C is not due to one of the above Ce^{3+} transitions, but may be due to the band-to-band transitions of the CYAM host crystal, or the optical transition from the Ce^{3+} ground state to the conduction band [10].

The decay time of the 430 nm fluorescence in CYAM:Ce was measured in the temperature range of 20–500 K. The decay time was 45 ns below 300 K, so that the optical transition is parity- and spin-allowed. However, the decay time above 300 K drastically decreased due to the thermal multiphonon-assisted nonradiative relaxation [9].

After removal of the UV light of 266 or 355 nm at 300 K, persistent phosphorescence was observed in spite of the fairly weak intensity compared with the Ce^{3+} fluorescence. The line shape of the persistent phosphorescence in Fig. 3 is in agreement with that of the Ce^{3+} fluorescence in Fig. 2.

Figure 4 shows the decay curves of the persistent

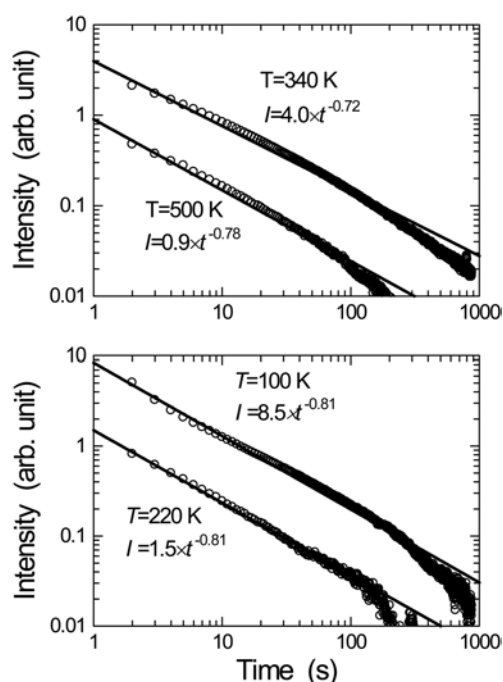


Fig. 4. Decay curves of the persistent phosphorescence in CYAM:Ce when measured at various temperatures in the time range from 1 to 1000 s.

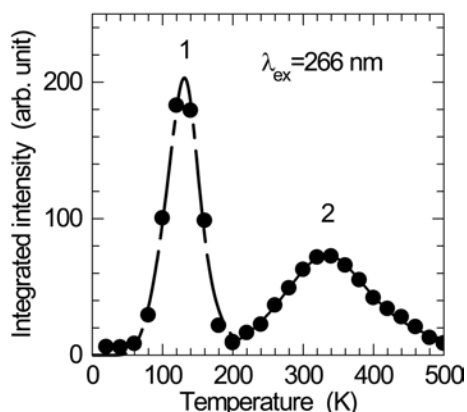


Fig. 5. Temperature dependence of total intensities of the integrated decay curves of the persistent phosphorescence from CYAM:Ce irradiated with the 266 nm light. The dash-dot and solid curves were calculated using Eq. (1) with fitting parameters (see the text).

phosphorescence at 430 nm after the 266 nm irradiation in the log-log scales at various temperatures. All decay curves do not fit to a single exponential function, but to t^{-n} power functions with n ($=0.7-0.8$) being slightly less than 1.

Figure 5 shows the total intensity of the integrated decay curve in the time range from 1 to 1000 s as a function of temperature. The total intensity consists of two components with peaks at 130 and 330 K, denoted by 1 and 2. The two components suggest, at least, two different recombination processes, resulting from the existence of two trapped electron and hole centers.

Figure 6 shows the afterglow curve of thermoluminescence

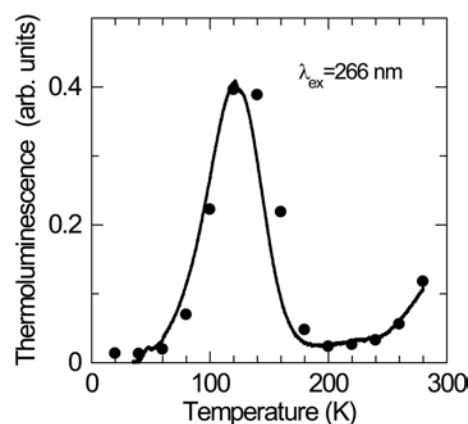


Fig. 6. Afterglow curve of thermoluminescence for CYAM:Ce. Solid circles are the data in Fig. 5.

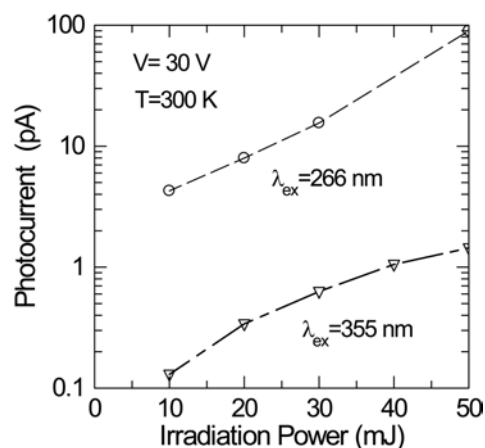


Fig. 7. Photocurrent in CYAM:Ce under the 266 nm or 355 nm excitation at 300 K.

(TL) in the temperature range 20–300 K [5]. This curve is in agreement with the component 1 of the persistent phosphorescence in Fig. 5.

Photoconductivity

Figure 7 shows photocurrents measured in CYAM:Ce under UV excitation at 300 K. The photocurrent under the 266 nm excitation is about fifty times larger than that under the 355 nm excitation. This result suggests that the energy levels of the excited states of Ce^{3+} corresponding to the 266 nm and 355 nm optical transitions are above and just below the bottom of the conduction band, respectively.

ESR

At first, the CYAM:Ce sample was irradiated with the 266 nm light at 300 K. After removal of the UV light, the sample temperature was immediately decreased to 77 K. Figure 8 shows the ESR spectrum of CYAM:Ce at 77 K composed of a single weak line with a g value of 2.002 and two sets of the sextet-hyperfine lines with a g value of 2.012. The sextet-hyperfine lines are due to the hyperfine coupling of electron spin with nuclear spin ($I = 5/2$) of Al. As the

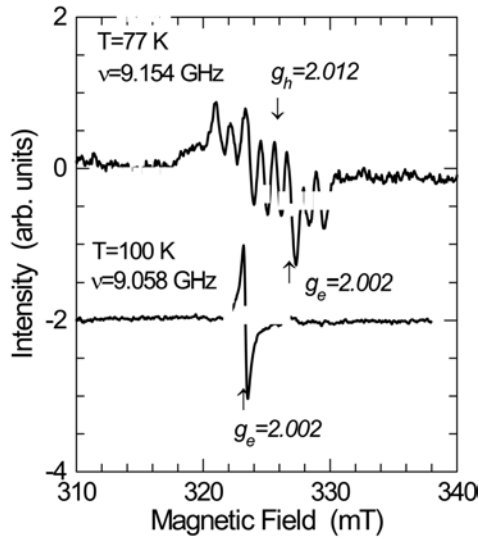


Fig. 8. ESR spectra observed in CYAM:Ce at 77 or 100 K.

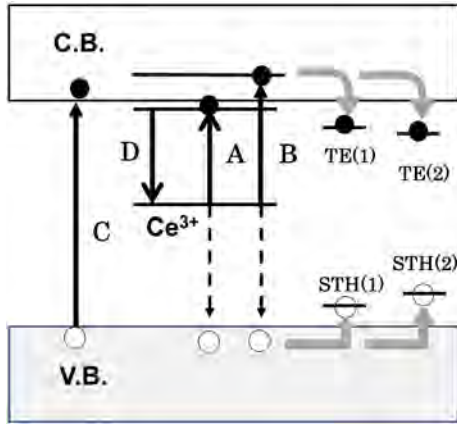


Fig. 9. A schematic energy diagram of CYAM:Ce. The energy level of the ground state of Ce^{3+} is lying in the middle of the band gap. Electron and hole centers, [TE(1), STH(1)], [TE(2), STH(2)] correspond to the components 1 and 2 in Fig. 5, respectively.

temperature was elevated up to 100 K, the sextet-hyperfine lines disappeared because of the spin-lattice relaxation and the single narrow line with $g = 2.002$ remains clearly visible. This single line is assigned to an electron trapped at an oxygen vacancy, which is stable below 300 K [6, 8]. These trapped charges correspond to the component 2 of the persistent phosphorescence in Fig. 5 because the irradiating temperature was 300 K.

Discussion

The line shape of the persistent phosphorescence is the same as that of the Ce^{3+} fluorescence. This result indicates that a hole, which is trapped at the activator Ce^{3+} in the form of Ce^{4+} , recombines radiatively by tunneling with a nearby trapped electron, namely, an electron trapped at an oxygen vacancy. The tunneling recombination between electrons and holes with their uniform distribution gives rise to the decay curve represented by the t^{-1} power function [5]. However, all

decay curves fit approximately to t^{-n} ($n = 0.7-0.8$) power functions [11]. The question is why the slope is a little smaller than that represented by t^{-1} .

We propose a model to account for such temperature dependence of the decay curves, including the ESR and photoconductivity results. Figure 9 shows a schematic energy diagram of Ce^{3+} in a wide band-gap oxide crystal, for example, CYAM:Ce. The energy level of the ground state of Ce^{3+} is lying in the middle of the band gap [12]. The absorption of two UV photons (see Fig. 9) can create electron-hole pairs in the crystal, resulting in the observation of the photocurrents in Fig. 7. In addition, the ESR analyses deduce that, after the UV irradiation, an electron is immediately trapped at an oxygen vacancy, whereas a hole is self-trapped at an Al^{3+} site [13]. Such ESR results are consistent with previous ESR studies of the persistent phosphors, CASM:Ce [6] and SAO:Eu [8], in which a hole is self-trapped in the forms of a single AlO_4 complex accompanied by a Si-vacancy and two adjacent AlO_4 complexes, respectively. Although self-trapped holes (STHs) are stable at low temperature [13], the STHs are mobile in the crystals and are trapped at Ce^{3+} in the form of Ce^{4+} when the temperature is elevated up to room temperature. With an assumption that a STH hops to an adjacent AlO_4 tetrahedron [11], the hopping rate of the STH represented by the Arrhenius equation increases with an increase of temperature [5]. This assumption can explain the enhancement of the components 1 and 2 of the persistent phosphorescence above 60 and 200 K in Fig. 5. However, the components 1 and 2 decrease rapidly above 130 and 330 K, respectively. Such quenching of the phosphorescence suggests a nonradiative decay process, that is, energy transfer to dark centers through thermal excitation of trapped electrons into the conduction band [5].

The intensity of the persistent phosphorescence including the radiative and nonradiative processes as a function of temperature is given by [11]

$$I(T) = \frac{I_0 \exp\left(-\frac{\Delta E_h}{kT}\right)}{1 + a \exp\left(-\frac{\Delta E_e}{kT}\right)}, \quad (1)$$

where a is a fitting constant and ΔE_e and ΔE_h are thermal activation energies, namely, the binding energies of trapped electron (TE) and STH as shown in Fig. 9. The numerator and denominator in Eq. (1) represent to the feeding and quenching rates of the intensity, respectively. The dash-dot and solid curves in Fig. 5 calculated using Eq. (1) and parameters of (ΔE_h (meV), ΔE_e (meV)) = $(35 \pm 5, 175 \pm 5)$ and $(100 \pm 10, 360 \pm 10)$ fit well to the components 1 and 2, respectively. The STHs and TEs related to the components 1 and 2 with the above different activation

energies are denoted by STH(1), STH(2), TE(1), and TE(2).

Finally, let us consider the origin of the two components 1 and 2 of the persistent phosphorescence using the energy diagram in Fig 9. When the temperature increases above 60 K, a STH(1) migrates to Ce^{3+} . The hole in the form of Ce^{4+} recombines with TE(1) by tunneling, resulting in emission from the component 1. Furthermore, the temperature increases above 130 K, then the TE(1) moves to a dark center through the thermal activation energy, resulting in quenching of the component 1. In the same way, the appearance and disappearance of the component 2 occurs when the temperatures increase from 200 to 500 K.

As shown in Fig. 1, there are three oxygen sites denoted by O(1), O(2) and O(3). O(2) is an apex of a tetrahedron, whereas O(1) or O(3) is shared between two tetrahedra. TE(1) or TE(2) may be assigned to an electron trapped at O(2) or [O(1), O(3)] vacancy, respectively. On the other hand, there are two aluminum sites, denoted by Al(1) and Al(2). The assignment of STH(1) and STH(2) to $\text{Al}(1)\text{O}_4$ and $\text{Al}(2)\text{O}_4$ complexes seems to be difficult because the observed binding energy of STH(2) is two times larger than that of STH(1). The STH structure in CASM:Ce was proposed to be an AlO_4 complex accompanied by a silicon vacancy [6]. Taking into account this result, STH(1) or STH(2) in CYAM may be assigned to a regular AlO_4 complex or an AlO_4 complex accompanied by a nearby aluminum vacancy.

Conclusions

Although the line shape of the persistent phosphorescence of Ce^{3+} in CYAM is the same as that of the fluorescence, the fairly long decay times of the persistent phosphorescence are distributed in the range of 1 to 1000 s. The photoconductivity under the UV excitation shows that electrons and holes created by the UV irradiation move in the conduction band and the valance band. On the other hand, the ESR spectra indicate that after the UV irradiation, an electron is

immediately trapped at an oxygen vacancy, whereas a hole is self-trapped around an Al^{3+} ion.

Although the TEs and STHs are stable at low temperatures, the electron-hole recombination at Ce^{3+} sites occurs by tunneling with an increase of temperature. Deficits in CYAM, namely, oxygen vacancies produced during the crystal growth process and the intrinsic defect related to STHs play an important role to persistent phosphorescence in CYAM:Ce.

Acknowledgment

One of the authors (M. Yamaga) is indebted to the Koshiyama Foundation for Promotion of Science and Technology for a research grant and Dr T.P.J. Han for the useful discussion.

References

1. G. Blasse, and B.C. Grabmaier, in "Luminescent Materials" (Springer, Berlin 1994) p. 1.
2. D.S. Hamilton, S.K. Gayen, G.T. Pogatschnik, R.D. Ghen, and W.J. Miniscalco, *Phys. Rev. B* [39] (1989) 8802-8815.
3. E.F. Schubert, in "Light-Emitting Diodes" (Cambridge University Press, Cambridge, 2006) p. 332-365.
4. J. Ueda, K. Aishima, S. Nishiura, and S. Tanabe, *Appl. Phys. Express* 4 [4] (2011) 042602-1-3.
5. S.W.S. Mckeever, in "Thermoluminescence of Solids" (Cambridge University Press, Cambridge, 1985) p. 143-148.
6. M. Yamaga, Y. Tanii, N. Kodama, T. Takahashi, and M. Honnda, *Phys. Rev. B* [65] (2002) 235108-1-10.
7. S.J. Louisnathan, *Can. Mineral.* 10 (1971) 822-837.
8. T. Takeyama, T. Nakamura, N. Takahashi, and M. Ohta, *Solid State Science* 6 [4] (2004) 345-348.
9. B. Henderson, and R.H. Bartram, in "Crystal-Field Engineering of Solid-State Laser Materials" (Cambridge University Press, 2000) Chaps. 6 and 10.
10. D. Jia, X. Wang, W. Jia, and W. M. Yen, *J. Lumin.* 119-120 (2006) 55-58.
11. M. Yamaga, Y. Masui, S. Sakuta, N. Kodama, and K. Kaminaga, *Phys. Rev. B* [71] (2005) 205102-1-7.
12. P. Dorenbos, *J. Lumin.* 122-123 (2007) 315-317.
13. K.S. Song, and R.T. Williams, in "Self-Trapped Excitons" (Springer-Verlag, Berlin, 1993) Chaps. 2 and 7.