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Persistent luminescence properties of monoclinic luminescent zirconium oxide annealed under different oxygen partial pressures

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Luminescent zirconium oxide (ZrO₂) with high purity (>3N) was annealed under different oxygen partial pressures ($P_{O_2} = 10^{-14}$ – 10^4 Pa) to investigate the effect of lattice defects on persistent luminescence (PersL). Although the Photoluminescence spectra profiles of samples (broad band emission centered at 485 nm) matched with the PersL spectra, PersL durations differed depending on the value of P_{O_2} during annealing. Samples annealed under a medium value of P_{O_2} such as 1 Pa tended to show long PersL duration. The two main trap levels were evaluated from thermoluminescence glow curves, and the ratio of two traps changed depending on the value of P_{O_2} during annealing. The time profiles of intensities of EPR signals (which assigned to F⁺-center and hole-trapped oxygen) were linked to the time profiles of luminescence intensities under and after ultraviolet irradiation. This result indicates that the F⁺-center and hole-trapped oxygen are involved in PersL.

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1. Introduction

Lattice defects are important factors for the design of materials with photo-functionalities such as photocatalysis and photochromism. In particular, the structure of the lattice defects is strongly related to persistent luminescence (PersL) properties.^{1,2)} PersL is a phenomenon whereby luminescence can last for minutes to hours after shutting off excitation light source. The phenomenon is considered to originate from dopants and lattice defects, which can store photo-excited electron or hole.³⁾ Thus, the control of lattice defects may lead to the design of materials with PersL properties.

In this study, we focused on luminescent zirconium oxide (ZrO₂) phosphor, which can show Photoluminescence (PL) and PersL without cation doping.⁴⁾ The luminescence properties of ZrO₂ have been studied from fundamental to application for decades.^{5–8)} This chemically stable and biocompatible material^{9,10)} has attracted the much attention in optical fields. In addition, much information on the crystal and defect structure of ZrO₂ has

been reported.^{11–13)} This information is useful for investigating the role of lattice defects in PersL. In general, ZrO₂ has three crystal phases: monoclinic, tetragonal and cubic phases. The monoclinic phase is stable at room temperature and shows a greenish-blue luminescence centered at 480–495 nm.^{14–16)} J. M. Carvalho et al. reported that the addition of titanium and lutetium ions to ZrO₂ has a strong effect on PersL properties.¹⁷⁾ S. V. Nikiforov's group observed an improvement in its luminescent properties by heat treatment under a reductive atmosphere (annealing in graphite crucibles).¹⁸⁾ The results of these studies suggest that oxygen defects play an important role in the PersL properties of ZrO₂.

In this study, ZrO₂ was annealed under different oxygen partial pressures ($P_{O_2} = 10^{-14}$ – 10^4 Pa) to investigate the effect of oxygen defects on PersL in more detail. Evaluation of crystal and defect structures was performed using X-ray powder diffraction and ultraviolet (UV) irradiating Electron paramagnetic resonance (EPR). PL, PersL decay curve and thermoluminescence (TL) glow curve were measured to determine the emission properties. Based on the data obtained from TL and UV irradiating EPR, we discuss the relationship between oxygen defects and PersL.

2. Experimental section

The raw material used in this study is ZrO₂ fine powder

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from Daiichi Kigenso Kagaku Kogyo Co., Ltd. The crystal phases are monoclinic and tetragonal (Supplementary data, Fig. S1). The crystallite size calculated by using the Scherrer formula for (1 1 -1) is approximately 10 nm. The natural impurity TiO_2 content is about 10 ppm. Other impurities include SiO_2 (100 ppm) and Fe_2O_3 (20 ppm). The powder in an alumina crucible was annealed at 1400 °C for 1 h under different P_{O_2} (monitored value: 1×10^4 , 10^3 , 10^2 , 10, 1, 10^{-6} , 10^{-9} , and 10^{-14} Pa) using a high-temperature furnace (SPM100-17V, Marusho Denki Co., Ltd.). We chose the 1400 °C as annealing temperature because the good luminescence properties of ZrO_2 annealed at this temperature was reported in some literature.^{18)–20)} A schematic diagram of the gas-flow system with O_2 sensor (C-48, Daiichi Nekk-ken Co., Ltd.) is given in Fig. S2. The P_{O_2} was controlled by adjusting the flow rate and concentrations of air, N_2 , and 3% H_2/N_2 gases. The P_{O_2} value is obtained from output gas. The heating rate was 10 °C/min, and the cooling was performed in the furnace. The X-ray powder diffraction patterns were measured using a Rigaku Ultima III (Cu- $K\alpha$ radiation). The diffraction angle (2θ) was scanned from 15 to 100° in 0.02° increments. In addition, Rietveld refinements of the samples were carried out with PDXL software (Rigaku Co.). PL and PersL decay curves were recorded on a spectrometer (FP-6500, JASCO Co.). PersL and PersLE (PersL excitation) spectra were obtained from the PersL decay curves with different excitation or detection wavelengths. TL glow curves were also recorded using fluorescence spectrometer with a cryostat (Janis Research Company, VPF-800) at a linear heating rate of 3 K/min in the temperature range between 220 and 400 K. Prior to the TL measurements, the samples were exited with 260 nm for 10 min at 200 K. UV (150W Xe-lamp, L9566-01A, Hamamatsu Photonics Co.) irradiating X-band EPR (EMX Nano, BRUKER Co.) was measured at room temperature in order to evaluate the defects structure of the samples.

3. Results and discussion

3.1 Characteristics of the materials

In general, when the oxygen partial pressure during annealing is decreased, more oxygen vacancies are introduced into oxide materials.^{21)–23)} In the obtained samples, it is predicted that the sample annealed under $P_{\text{O}_2} = 10^4$ Pa has the smallest amount of oxygen vacancies and that the sample annealed under $P_{\text{O}_2} = 10^{-14}$ Pa has the largest amount of oxygen vacancies. X-ray diffraction patterns showed that the phase of all samples was monoclinic (Fig. S3). It was shown that tetragonal or cubic phase of ZrO_2 can be stabilized by the presence of excess oxygen vacancies.²⁴⁾ However, the samples obtained in this process (annealing under various values of P_{O_2}) were single-phase monoclinic. **Figure 1** shows Rietveld refinements of the samples annealed under maximum P_{O_2} (10^4 Pa) and minimum P_{O_2} (10^{-14} Pa). The reliability factors of calculation ($P_{\text{O}_2} = 10^4$ and 10^{-14} Pa) were $R_{\text{wp}} = 5.77$ and 5.79%, $S = 1.27$ and 1.29. The obtained lattice constants in both samples were identical ($a = 0.515$ nm, $b = 0.521$ nm, $c =$

Fig. 1. X-ray powder diffraction patterns and Rietveld refinement profiles for ZrO_2 annealed under (a) $P_{\text{O}_2} = 10^4$ Pa and (b) $P_{\text{O}_2} = 10^{-14}$ Pa.

0.531 nm, and $\beta = 99.2^\circ$). The crystallite sizes calculated by using the Scherrer formula for (1 1 -1) of the samples annealed under $P_{\text{O}_2} = 10^4$ and 10^{-14} Pa were almost same (~ 30 nm). These values are larger than that of the raw ZrO_2 powder (approximately 10 nm). The increase of crystallite size after annealing indicates that crystallite growth occurred under various P_{O_2} . From this result, it is predicted that oxygen vacancies also exist inside of the crystal.

In order to investigate the state of lattice defects, we measured UV irradiating EPR spectra for samples annealed under $P_{\text{O}_2} = 10^4$, 1 and 10^{-14} Pa (**Fig. 2**). With UV irradiation, the three main signals (I, II and III) were observed in all samples. Although the signal I in $P_{\text{O}_2} = 10^4$ Pa sample was somewhat difficult to detect at room temperature, it was clearly observed at 250 K (Fig. S4). In the following discussion, we consider that signal I ($g: 2.011$), signal II ($g: 1.990$) and signal III ($g: 1.976$) are assigned to hole-trapped oxygen, F^+ -center (oxygen vacancy trapped one electron) and Zr^{3+} .^{25)–27)} Before UV irradiation, mainly Zr^{3+} was observed. The amounts of Zr^{3+} were decreased by reductive annealing. Zr^{3+} is expected to be changed to Zr^{2+} or Zr^{4+} by high temperature annealing under reductive condition.^{19),25)} This change is likely to influence the charge valence of oxygen vacancies around the zirconium ion. Hole-trapped oxygen and F^+ -centers were generated by UV irradiation. The amounts of F^+ -centers reached a maximum in sample annealed under medium P_{O_2} (1 Pa). These results indicate that P_{O_2} during annealing affects the state of

lattice defects (i.e., charge valence, coordination environment). Accordingly, we obtained samples that have the same crystal structure and different states of oxygen vacancies.

3.2 PL and PersL properties

PL and PL excitation (PLE) spectra of obtained monoclinic ZrO_2 are shown in Fig. 3(a). PL spectra of all samples showed broad band emission centered at 485 nm. This indicates that the samples annealed under various values of P_{O_2} have a common emission center. There are two candidates of the emission center in monoclinic ZrO_2 . One is titanium ion²⁰⁾ contained as an impurity, and the other is oxygen vacancies.²⁸⁾ The difference in PL intensities of the samples was not large (Fig. S5). Figure 3(b) shows PersL (after excitation was stopped for 10 s) and PersLE spectra. PersL spectra profiles of the samples match with those of PL. In addition, the shape of PersL spectra after excitation stopped for 1, 5, and 10 s was same (Fig. S6). These results indicate that PL and PersL were from the same

emission center. PersLE spectra were red-shifted compared to those of PL. This suggests that lower energy excitation is effective for carrier trap.

Figure 4(a) shows PersL decay curves of ZrO_2 annealed under $P_{\text{O}_2} = 10^4$, 1 and 10^{-14} Pa. Profiles of decay curves changed with different values of P_{O_2} during anneal-

Fig. 2. Before (solid line) and under UV irradiating (dashed line) EPR spectra for ZrO_2 annealed under (1) $P_{\text{O}_2} = 10^4$ Pa, (2) $P_{\text{O}_2} = 1$ Pa, and (3) $P_{\text{O}_2} = 10^{-14}$ Pa.

Fig. 3. (a) PL and PLE spectra for ZrO_2 annealed under $P_{\text{O}_2} = 10^4$, 1, and 10^{-14} Pa. (b) PersL (after excitation was stopped for 10 s) and PersLE spectra for ZrO_2 annealed under $P_{\text{O}_2} = 10^4$, 1, and 10^{-14} Pa.

Fig. 4. (a) PersL decay curves ($\lambda_{\text{em}} = 485$ nm) at room temperature for ZrO_2 annealed under $P_{\text{O}_2} = 10^4$, 1, and 10^{-14} Pa. The samples were excited at 300 nm for 5 min before recording. (b) PersL duration times (until intensity < 10 : orange dots and intensity < 100 : black dots) at room temperature for ZrO_2 annealed under different oxygen partial pressures.

Fig. 5. TL glow curves ($\lambda_{\text{em}} = 485 \text{ nm}$) for ZrO_2 annealed under (1) $P_{\text{O}_2} = 10^{-4} \text{ Pa}$, (2) $P_{\text{O}_2} = 1 \text{ Pa}$, and (3) $P_{\text{O}_2} = 10^{-14} \text{ Pa}$ recorded at the rate of 3 K/min, after exciting the samples at 260 nm for 10 min (at 200 K). Decomposition of the main peak into two Gaussian functions (A and B).

ing (PersL decay curves of all samples were shown in Fig. S7). The sample annealed under $P_{\text{O}_2} = 1 \text{ Pa}$ showed the highest PersL intensity (after excitation was stopped for 1 min) of all samples. PersL duration times (until intensity <100 and 10) were plotted against P_{O_2} during annealing [Fig. 4(b)]. The PersL duration times tended to be longer at medium values of P_{O_2} such as 1 Pa. The same behavior was observed in the samples annealed at 1400 °C for 6 h under different P_{O_2} (Fig. S8). These results suggest that the PersL duration of ZrO_2 does not always increase with an increase of oxygen vacancies.

In order to investigate the trap levels of the samples that showed different PersL properties, TL glow curves were recorded (Fig. 5). In all samples, a main peak was observed in the range of 220–300 K. The main peak in all samples could be decomposed by curve fitting with two Gaussian functions (A and B in the Fig. 5). The depths of trap A and trap B were evaluated to be 0.37 and 0.42 eV, respectively, by using the Hoogenstraaten method (heating rate = 3, 5, and 7 K/min).²⁹⁾ Trap B has a strong influence on PersL at room temperature. The trap ratio (B/A) changed depending on the value of P_{O_2} . These results indicate that the value of P_{O_2} during annealing affects the number of traps. We succeeded in changing the number of traps, which are effective for PersL, by controlling P_{O_2} during annealing. The trap ratio reached a maximum with annealing under $P_{\text{O}_2} = 1 \text{ Pa}$. This trend is related to the amount of F^+ -centers in the samples under UV irradiation. This suggests that the F^+ -center is related to trap B. On the other hand, the trap A is not associated with a specific EPR signal. The reason for this is thought to be that trap A arise from EPR silent defects such as F-center (oxygen vacancy trapped two electron).

3.3 Relationship between lattice defects and PersL

We have reported the EPR measurement of ZrO_2 at 4 K and observed the formation of F^+ -center by UV irradiation.¹⁹⁾ These results clearly indicated the effects of F^+ -center on PersL. In this study, we focus on the time dependence of specific EPR signal at room temperature to investigate the relationship between carrier trap/release of oxygen defects and PersL. All measurements were con-

Fig. 6. EPR spectra at room temperature for ZrO_2 annealed under $P_{\text{O}_2} = 1 \text{ Pa}$ (1) before UV irradiation, (2) under UV irradiation (3 min after starting UV irradiation), (3) 3 min after shutting off UV irradiation, and (4) after heat treatment at 450 K.

ducted using the sample annealed under $P_{\text{O}_2} = 1 \text{ Pa}$, which showed the highest PersL intensity (after excitation was stopped for 1 min). EPR spectra was measured before UV irradiation, under UV irradiation (3 min after starting UV irradiation), 3 min after shutting off the UV irradiation, and after heat treatment at 450 K (Fig. 6). The difference in signal III intensities under and after UV irradiation was small. Signal I and signal II were generated by UV irradiation and decreased after shutting off the UV irradiation. Some parts of signal I and signal II remained 3 min after shutting off the irradiation. The remaining signals were extinguished by heat treatment at 450 K.

Figure 7(a) shows the time profiles of intensities of EPR signals (signal I and signal II) at room temperature. Immediately after starting the irradiation, the intensities of signal I and signal II increased rapidly. The increase of signal intensities per unit time gradually decreased with increase in the excitation time. After shutting off the UV irradiation, the signal intensities decreased gradually. The behavior of the signals under and after UV irradiation is similar to the time profile of luminescence intensity [Figs. 7(b) and 7(c)]. When irradiating the excitation light source on PersL materials, luminescence intensity

Fig. 7. (a) Time profiles of intensities of EPR signals at room temperature for ZrO_2 annealed under $P_{\text{O}_2} = 1$ Pa. (b) Time profiles of luminescence intensity ($\lambda_{\text{em}} = 485$ nm) under excitation light at 300 nm for ZrO_2 annealed under $P_{\text{O}_2} = 1$ Pa. (c) PersL decay curve ($\lambda_{\text{em}} = 485$ nm) at room temperature for ZrO_2 annealed under $P_{\text{O}_2} = 1$ Pa. The sample was excited at 300 nm for 60 s before recording.

increases until completion of career trap because the processes of emission and career trap occur simultaneously. After shutting off the irradiation, only career release from the traps gradually occurred. Thus, the results of Fig. 7 indicate that signal I and signal II are linked to the process of career trap and release at room temperature.

As mentioned in section 3.1, we consider that signal I, signal II and signal III are assigned to hole-trapped oxygen, F^+ -center and Zr^{3+} .^{25)–27)} Zr^{3+} is probably not involved in PersL at room temperature because signal III hardly changed after shutting off the UV irradiation. The time profiles of intensities of EPR signals (Signal I and signal II) suggest that the F^+ -center and hole-trapped oxygen are involved in PersL at room temperature. This also supports the possibility that the F^+ -center is related to trap B. For the above reasons, the amount of F^+ -centers during UV irradiation is important for the PersL duration of ZrO_2 . Parts of signal I and signal II remained after shutting off the irradiation were not involved in PersL at room temperature. These signals are likely to be related to the traps that release the career at a temperature above room temperature because these signals were extinguished by heat treatment at 450 K. To test this hypothesis, high-temperature EPR measurements and more detailed analysis are required.

4. Conclusions

In the present work, PersL properties of ZrO_2 annealed under various values of P_{O_2} were investigated. The samples obtained in this process had the same average crystal

structure and different states of oxygen vacancies. PL and PersL of all samples were from the same emission center. The profiles of PersL decay curves were changed by different values of P_{O_2} during annealing. The samples annealed under medium P_{O_2} such as 1 Pa tended to show a long PersL duration. The two main trap levels were evaluated from TL glow curves in the samples. The number of deeper traps reached a maximum with annealing under medium P_{O_2} . This contributes to an increase in PersL duration at room temperature. The time profiles of EPR signals under and after UV irradiation suggested that the F^+ -center and hole-trapped oxygen are related to PersL. The findings in this study are expected to be useful for the control of PersL properties of oxide phosphor.

References

- 1) Z. Pan, Y. Y. Lu and F. Liu, *Nat. Mater.*, **11**, 58–63 (2012).
- 2) Z. Liu, X. Jing and L. Wang, *J. Electrochem. Soc.*, **154**, 440–443 (2007).
- 3) Y. Li, M. Gecevicius and J. Qiu, *Chem. Soc. Rev.*, **45**, 2090–2136 (2016).
- 4) Y. Cong, B. Li, B. Lei and W. Li, *J. Lumin.*, **126**, 822–826 (2007).
- 5) J. F. Sarver, *J. Electrochem. Soc.*, **113**, 124–128 (1966).
- 6) P. Iacconi, D. Lapraz and R. Caruba, *Phys. Status Solidi*, **50**, 275–283 (1978).
- 7) S. Nakayama, I. Nitani, T. Asahi, M. Shiomi and T. Miyata, *J. Ceram. Soc. Jpn.*, **124**, 950–953 (2016).
- 8) S. Goto, Y. Takahashi, N. Terakado, Y. Nakajima, N. Onoue, T. Shinozuka and T. Fujiwara, *J. Ceram. Soc. Jpn.*, **127**, 696–699 (2019).
- 9) T. S. Jeon, J. M. White and D. L. Kwong, *Appl. Phys. Lett.*, **78**, 368–370 (2001).
- 10) M. N. Tahir, R. Ragg, F. Natalio, J. K. Sahoo, P. Daniel, K. Koynov, D. Strand, S. Strand and W. Tremel, *J. Mater. Chem. B*, **3**, 2371–2377 (2015).
- 11) T. V. Perevalov and D. R. Islamov, *Microelectron. Eng.*, **178**, 275–278 (2017).
- 12) C. Imparato, M. Fantauzzi, C. Passiu, I. Rea, C. Ricca, U. Aschauer, F. Sannino, G. D’Errico, L. DeStefano, A. Rossi and A. Aronne, *J. Phys. Chem. C*, **123**, 11581–11590 (2019).
- 13) J. Matta, J. F. Lamonier, E. Abi-Aad, E. A. Zhilinskaya and A. Aboukaïs, *Phys. Chem. Chem. Phys.*, **1**, 4975–4980 (1999).
- 14) L. Puust, V. Kiisk, K. Utt, H. Mändar and I. Sildos, *Cent. Eur. J. Phys.*, **12**, 415–420 (2014).
- 15) Y. Nobuta, Y. Takahashi, T. Miyazaki, N. Terakado, N. Onoue, T. Shinozaki and T. Fujiwara, *J. Ceram. Soc. Jpn.*, **125**, 343–347 (2017).
- 16) V. Kiisk, L. Puust, K. Utt, A. Maaros, H. Mändar, E. Viviani, F. Piccinelli, R. Saar, U. Joost and I. Sildos, *J. Lumin.*, **174**, 49–55 (2016).
- 17) J. M. Carvalho, L. C. V. Rodrigues, J. Hölsä, M. Lastusaari, L. A. O. Nunes, M. C. F. C. Felinto, O. L. Malta and H. F. Brito, *Opt. Mater. Express*, **2**, 331–340 (2012).
- 18) S. V. Nikiforov, V. S. Kortov, A. N. Kiryakov, S. F. Konev and A. A. Men’shenina, *Tech. Phys. Lett.*, **43**, 1074–1076 (2018).

- 19) K. Iwasaki, Y. Takahashi, N. Terakado, N. Onoue, T. Shinozaki and T. Fujiwara, *Ceram. Int.*, **44**, 12929–12933 (2018).
- 20) Z. Wang, J. Zhang, G. Zheng, Y. Liu and Y. Zhao, *J. Lumin.*, **132**, 2817–2821 (2012).
- 21) B. D. C. Bell, S. T. Murphy, P. A. Burr, R. W. Grimes and M. R. Wenman, *J. Appl. Phys.*, **117**, 084901 (2015).
- 22) H. Liu, F. Zeng, Y. Lin, G. Wang and F. Pan, *Appl. Phys. Lett.*, **102**, 181908 (2013).
- 23) H. Luo, Y. Shin, Y. Yu, D. Cetin, K. Ludwig, U. Pal, S. N. Basu, S. Gopalan and X. Lin, *Appl. Surf. Sci.*, **323**, 65–70 (2014).
- 24) S. Fabris, A. T. Paxton and M. W. Finnis, *Acta. Mater.*, **50**, 5171–5178 (2002).
- 25) E. V. Frolova and M. I. Ivanovskaya, *Mater. Sci. Eng., C*, **26**, 1106–1110 (2006).
- 26) J. A. Phys, S. Wright and R. C. Barklie, *J. Appl. Phys.*, **106**, 103917 (2012).
- 27) C. Gionco, M. C. Paganini, E. Giamello, R. Burgess, C. Di Valentin and G. Pacchioni, *Chem. Mater.*, **25**, 2243–2253 (2013).
- 28) T. V. Perevalov, D. V. Gulyaev, V. S. Aliev, K. S. Zhuravlev, V. A. Gritsenko and A. P. Yelisseyev, *J. Appl. Phys.*, **116**, 2–6 (2014).
- 29) W. Hoogenstraaten, *Philips Res. Rep.*, **13**, 515–693 (1958).