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Study on effects of carbon impurities and oxygen vacancies in amorphous alumina phosphor prepared via a solution method

Yoshinori Wakui^a, Kanako Takahashi^a, Yue Jin Shan^{a,*}, Keitaro Tezuka^a, Hideo Imoto^a, Shogo Hosokawa^b, Norifumi Shinozaki^b, Mariko Ando^c, Hideki Maekawa^c

^a Department of Material and Environmental Chemistry, Graduate School of Engineering, Utsunomiya University, 7-1-2 Yoto, Utsunomiya-shi, Tochigi 321-8585, Japan

^b Tatsumori Ltd., 50 Minami-Kawada, Kami-Yukiai, Tamura-cho, Koriyama-shi, Fukushima 963-0724, Japan

^c Graduate School of Engineering, Tohoku University, 6-6-04 Aramaki Aoba, Sendai-shi, Miyagi 980-8579, Japan

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ABSTRACT

The amorphous alumina phosphors without containing expensive or toxic elements were prepared via a solution method. The obtained sample indicates bluish-white emission centered at 390–430 nm by UV excitation. According to the measurement results of Electron Spin Resonance (ESR), Fourier Transform Infrared Spectroscopy (FT-IR) and organic microanalysis, it is found that the carbon impurities exist in the sample and they are essential for luminescence. On the other hand, ²⁷Al NMR measurements indicate the presence of Al of 5-coordination. Moreover, there is good correspondence among the excitation spectra of the emission samples, the experimental optical properties of amorphous alumina, and the calculated oxygen vacancies levels in amorphous alumina model. Therefore, the new luminescence mechanism can be proposed as follows; the electrons in the valence band are excited to oxygen vacancies bands by UV light and return to ground state through the carbon impurities band, being accompanied by the bluish-white emission.

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1. Introduction

In modern society, luminescent materials play an important role for information displays and lighting [1]. In general, most of inorganic phosphors used in commercial way are compounds containing expensive rare earth or toxic elements as luminescence center. Therefore, it is required to synthesize rare earth free and environment friendly fluorescent materials. From more than 10 years before, some amorphous alumina fluorescent materials have been reported as rare earth free phosphor. This kind of amorphous alumina phosphor has been prepared by a sol-gel method [1–4], anodization method [5–7], ultrasonic spray pyrolysis method [8] and so on. All of these alumina phosphors were in an amorphous state, had a broad emission peak in the range of 390–450 nm, and the fluorescence intensity decreased or disappeared with appearing or increasing the peaks on their XRD patterns.

The luminescent mechanism of these alumina phosphors has been expected to oxygen vacancies and carbon related impurities arising from raw materials. However, there are not enough evidences to confirm these two estimated origins, so the luminescent mechanism does not become clear. Accordingly, it would be of great interest

and importance to investigate the luminescence mechanism of amorphous alumina phosphor. We succeeded in preparing the amorphous alumina fluorescent substances by a very simple and easy solution method. Our synthetic method is similar to the sol gel process in what has been reported. Lin et al. reported the alumina powder samples prepared via a pechini-type sol-gel method, which had an emission peak wavelength around 430 nm [1]. Kurokawa et al. prepared the transparent alumina films by the sol-gel method, which emitted the light in 390–430 nm [2]. Yoldas released the alumina sample made from aluminum sec-butoxide via the sol-gel method, which showed an emission peaking at ~425 nm with a shoulder at ~475 nm [3]. On the other hand, our sample has broad excitation spectrum with several peaks in less than 390 nm and has broad fluorescence spectrum with a peak around 390–430 nm. When these luminescence features and synthetic procedures are taken into consideration, our sample has probably the same luminescence origin as the alumina phosphors prepared by others.

In this paper, we examined the luminescence mechanism through mainly analyzing two samples obtained from the solution method, which had approximately similar crystal characteristics and extremely different PL intensities. Moreover, additional experiments were conducted to confirm the influence of carbon impurities and oxygen vacancies. Finally, we proposed a new luminescence mechanism for the amorphous alumina phosphor prepared by the solution method.

* Corresponding author. Tel.: +81 28 689 6174; fax: +81 28 689 6174.

E-mail address: shan@cc.utsunomiya-u.ac.jp (Y.J. Shan).

Table 1
Synthetic conditions of the emission sample (AO_{em}) and the feeble emission sample (AO_{f-em}) used for elucidation of luminescence mechanism.

	Preheating condition	Sintering condition
AO _{em}	300 °C, 7 h	650 °C, 5 h
AO _{f-em}		700 °C, 5 h

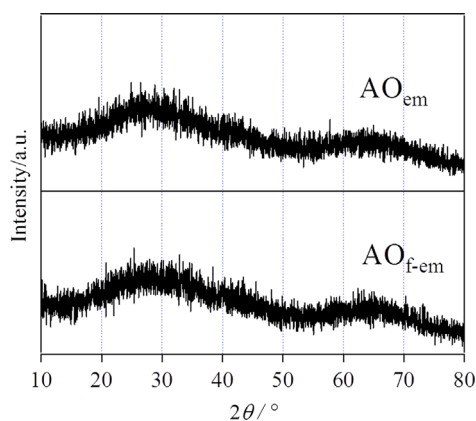


Fig. 1. XRD patterns of AO_{em} and AO_{f-em}.

2. Experimental

Amorphous alumina powder samples were prepared via the solution method. Typically, 3.7513 g of Al(NO₃)₃·9H₂O was dissolved in 3.8 mL diethylene glycol by heating and stirring on the hotplate at 110 °C for 10 min (the molar ratio of Al to DEG was 1:4). The obtained mixed solution was preheated at 300–350 °C for 3–7 h, and then sintered at 650–730 °C for 2–5 h. Table 1 shows the synthetic conditions of two samples of AO_{em} and AO_{f-em}, and the investigation of luminescence mechanism is carried out through mainly analyzing and comparing the nature of AO_{em} and AO_{f-em}.

All samples were characterized by the X-ray diffraction (XRD) on a Rigaku RINT-2200 diffractometer with monochromatized Cu K α radiation ($\lambda=0.15418$ nm). Excitation and emission spectra were taken on a JASCO FP-6500 spectrofluorometer equipped with a 150 W Xenon Lamp as the excitation source and JASCO ISF-513 integrating sphere. CHN-Elemental Analysis (CHN-EA) was performed on a PerkinElmer Japan 2400II analyzer. FT-IR spectra were recorded on a JASCO FT/IR4100 infrared spectrophotometer using the KBr plate method. ²⁷Al NMR measurements were performed on a JEOL RESONANCE ECA600 FT NMR spectrometer operated at 156.39 MHz. Electron spin resonance (ESR) spectra were observed on a JEOL JES-TE100 electronic spin resonance spectrophotometer. Ultraviolet-visible (UV-vis) reflectance spectra were acquired on a JASCO V-570 UV-vis spectrometer. Thermogravimetry-Differential Thermal Analysis (TG-DTA) was taken under air flow (flux of 100 mL min⁻¹) with a Bruker AXS TG-DTA2000S apparatus, at a heating rate of 20 °C min⁻¹, with Al₂O₃ as a reference. TG-DTA-Mass Spectrometry (MS) was performed with a Rigaku Thermo Mass/Photo.

3. Results and discussions

3.1. Characteristics of two samples used for the study of luminescence mechanism

XRD patterns and Photoluminescence/Photoluminescence Excitation (PL/PLE) spectra of AO_{em} and AO_{f-em} are exhibited in Figs. 1 and 2, respectively. As shown in Fig. 1, neither of them

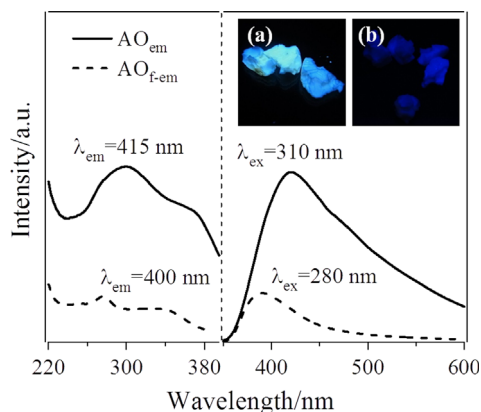


Fig. 2. PL/PLE spectra of AO_{em} and AO_{f-em}. The insets (a) and (b) are luminescent photographs of AO_{em} and AO_{f-em}, under the excitation of 365 nm UV light, respectively.

has a diffraction peak, and this indicates that they are in amorphous state. On the other hand, AO_{em} and AO_{f-em} are different in fluorescence property (see Fig. 2 and insets). AO_{em} shows the broad emission band with a peak at 421 nm. The corresponding PLE spectrum has broad excitation band with a peak at 299 nm and shoulder around 370 nm, and seems to have excitation band in less than 220 nm (220 nm is lower detection limit of spectrofluorometer). AO_{f-em} shows the weak broad emission band with a peak at 391 nm. The corresponding PLE spectrum has broad excitation band with a peak at 277 nm and shoulder around 350 nm, and seems to have excitation band in less than 220 nm. As shown in Fig. 2 insets, AO_{em} shows bluish-white emission but AO_{f-em} shows feeble blue emission under UV-lighting excitation.

3.2. Investigation of unpaired electron

Luminescent property is deeply related to electron transfer in material. In general, unpaired electron can cause the transition; thus it is thought that unpaired electron is concerned with the luminescence of amorphous alumina phosphor. On the other hand, unpaired electrons can be detected and characterized sensitively and quantitatively by the Electron Spin Resonance (ESR) techniques [9]. Actually, ESR signals observed in amorphous alumina phosphor have been reported so far [1,3,9–12]. Lin et al. considered that strong and sharp ESR signal around $g=2.02$ would be derived from carbonyl defects in their samples, and presumed that these carbonyl defects could be a luminescence center [1]. Yoldas observed weak signals at $g=2.0058$ in alumina sample and considered that this signal would originate from paramagnetic state of oxygen vacancies, and he also detected strong signals at $g=2.0031$ for AlSiO_{3.5}, and 2.0053 for Al₃SiO_{6.5}, which would be derived from carbon impurities [3]. Moreover, F⁺ center (oxygen vacancies occupied by one electron) may be able to be discerned by ESR. Du et al. thought that EPR signal at $g=2.0085$ was derived from F⁺ center, and supposed it to be a luminescence center [12].

ESR spectra of AO_{em} and AO_{f-em} are shown in Fig. 3. There is a strong signal at $g=2.004$ in the spectrum of AO_{em}, but seems to be hardly observed in that of AO_{f-em}. This indicates that the emission of our sample is related to some kind of paramagnetic defects. In order to conduct more detailed investigation about unpaired electrons, samples with different luminescence intensities were prepared by preheating at 350 °C for 3 h and sintering at 730 °C for several hours, and their ESR spectra were measured. These samples are represented by labels of AO730- x (x is sintering hour). The PL/PLE spectra of AO730- x are shown in Fig. 4. Their PL intensities are changed depending on the sintering time and AO730_3 indicates the strongest emission. The ESR spectra of

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