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Long lasting phosphorescence properties of Tb³⁺-activated reduced calcium aluminate glasses

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Abstract. A long lasting green phosphorescence was found in Tb³⁺-doped calcium aluminate glasses prepared under a strongly reducing atmosphere. An electron-trapped centre giving an EPR signal at $g = 1.999$, an analogue of the F⁺ centre in CaO, was induced by illumination with ultraviolet (uv) radiation and decayed slowly after the illumination was stopped. A partial oxidation of Tb³⁺ ions to Tb⁴⁺ ions by uv illumination was observed. A mechanism of the long lasting phosphorescence was suggested to consist of recombination of an electron released thermally from the F⁺-like centre with the photo-oxidized Tb³⁺ (Tb⁴⁺).

1. Introduction

Long lasting phosphorescent materials are used in a variety of applications such as luminescent paints. Several crystalline materials are known so far, i.e., ZnS:Cu and SrAl₂O₄:Eu²⁺ [1]. Recently, Matsuzawa *et al* [2] found that SrAl₂O₄:Eu²⁺, Dy³⁺ shows very intense and long lasting green phosphorescence and proposed a mechanism. According to this model, the phosphorescence is ascribed to the photoconductivity due to positive holes, and to the trapping and thermal release of the holes by Dy³⁺ ions in the system. Here we report new long lasting phosphorescent glasses, reduced calcium aluminate glasses activated with Tb³⁺ ions, and suggest a possible mechanism consisting of photoionization of Tb³⁺ ions and recombination of the photo-oxidized Tb³⁺ ions (Tb⁴⁺) and the electrons thermally released from F⁺-like centres.

2. Design of mechanism and materials

There is a narrow glass formation range in the binary system CaO–Al₂O₃, CaO; 62–65 mol%. The resulting glasses have unique properties [3–6] that are associated with oxygen-related structural defects, depending on the melting atmosphere. Glasses prepared in an ambient atmosphere, which are called ‘oxidized’ glasses, exhibit high photosensitivity to deep ultraviolet radiation [3] and a marked O₂-effervescence upon heating [4]. On the other hand, when the glasses are remelted under strongly reducing conditions, the resulting glasses, which are called ‘reduced’ glasses, exhibit phototropy [7]. Here, we focus on this

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phenomenon. Upon exposure to uv radiation, broad absorptions peaking around 2 eV are induced, and after interruption of the illumination the absorptions fade at room temperature. The origin of this phototropy is ascribed to the formation of an electron trapped at the site of oxygen vacancy surrounded by Ca^{2+} ions produced during melting under strongly reducing conditions. This electron-trapped centre is an analogue of the F^+ centre (an electron trapped at the site of O^{2-} vacancy) in CaO and gives a nearly symmetric EPR signal at $g = 1.998$ [8].

It is our idea to impart long lasting phosphorescence properties to reduced calcium aluminate glasses by combining this F^+ -like centre with an appropriate phosphor. Requirements for a phosphor in the combination of the electron-trapped centre are twofold: one is a redox valence-alternative property. Long lasting phosphorescence originates from hole-trapped phosphor ions by capturing an electron thermally released from the electron centres. Thus, a valence-alternative phosphorescent ion is required. In other words, the oxidized valence state of the phosphor must be stable so as to be able to trap a positive hole. Another requirement is related to the following fact. It is required that phosphorescence is emitted from the low valence state of the valence-alternative phosphor ion which traps a photo-generated positive hole. Since the precursor of the F^+ -like centre, an oxygen vacancy, is produced by strongly reducing treatment, the majority of the phosphor ions takes a low valence state. Thus, this requirement needs to be met. We choose Tb ions as an appropriate phosphor in the present work because they take +3 (electronic configuration $[\text{Xe}]4f^8$) and +4 charge states ($[\text{Xe}]4f^7$) and a green emission due to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition in Tb^{3+} (low valence state) is the main phosphorescence.

3. Experiment

The chemical composition of the glasses is $59 \text{ CaO} \cdot 27 \text{ Al}_2\text{O}_3 \cdot 7 \text{ SiO}_2 \cdot 7 \text{ MgO}$ in mol%. This is a modified composition of $63 \text{ CaO} \cdot 37 \text{ Al}_2\text{O}_3$ glasses. The addition of SiO_2 and MgO to the base composition is known to facilitate stable glass formation by conventional melt-quenching [9]. No significant difference between these two glasses was seen for the results which will be described hereafter. High purity chemical reagents ($>4 \text{ N}$) of CaCO_3 , Al_2O_3 , SiO_2 and MgO were used as starting materials. Terbium ions were added to the batches at the concentration of 0.1 mol% as Tb_4O_7 . Carefully mixed batches were sintered at 1200°C for 1 h and melted in alumina crucibles at 1450°C for 0.5 h in air. Melts were poured onto a stainless steel plate and pressed with a stainless plate. The resulting 'oxidized' glasses were put into graphite crucibles and remelted at 1550°C for 4 h. The melt was quenched similarly and annealed at $\sim 800^\circ\text{C}$. The resulting glasses are referred to the 'reduced' glasses so as to discriminate from the 'oxidized' glasses.

The resulting glasses were cut into rectangular plates ~ 2 mm thick and optically polished. Optical absorption and photoluminescence spectra of the specimens were measured at room temperature with a conventional spectrophotometer and a fluorescence photometer, respectively. Decay of photoluminescence was measured by monitoring the intensity of the intense emission band from the specimen mounted in the sample room of the fluorescence photometer. Light-induced electron paramagnetic resonance (EPR) spectra of the specimen were measured with a Bruker model 360E spectrometer at $\sim 300 \text{ K}$. The specimen was illuminated with 254 nm light (intensity, 1.7 mW cm^{-2}) from a filtered Xe/Hg lamp through an optical window of the microwave cavity.

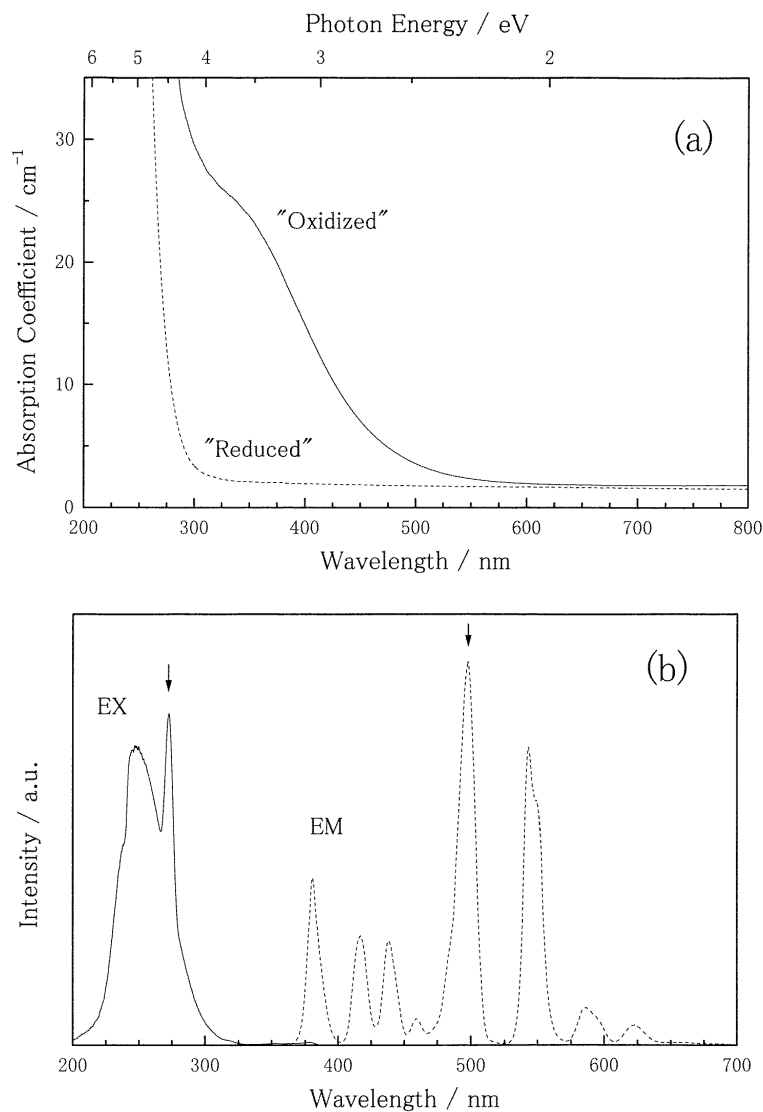


Figure 1. (a) Optical absorption spectra of calcium aluminate glasses doped with 0.1 mol% of Tb₄O₇. —, 'oxidized' glass (melted in air), - - -: 'reduced' glass (melted in carbon crucible). (b) Photoluminescence spectra of reduced calcium aluminate glasses doped with Tb ions. EM: photoemission spectrum upon excitation with 254 nm light, EX: photoexcitation spectrum for the peak at 543 nm (⁵D₄ → ⁷F₅). The bands indicated by arrows are due to second or 1/2 order diffraction.

4. Results and discussion

Figure 1(a) shows optical absorption spectra of the 'oxidized' and 'reduced' glasses. A broad absorption band peaking at ~350 nm is seen for the 'oxidized' glasses. No such band is seen for the 'reduced' glasses. Colours of the 'oxidized' and 'reduced' glasses are yellowish brown and colourless, respectively. The peak position (~350 nm) and broad width of the absorption agree well with the features of the charge transfer band

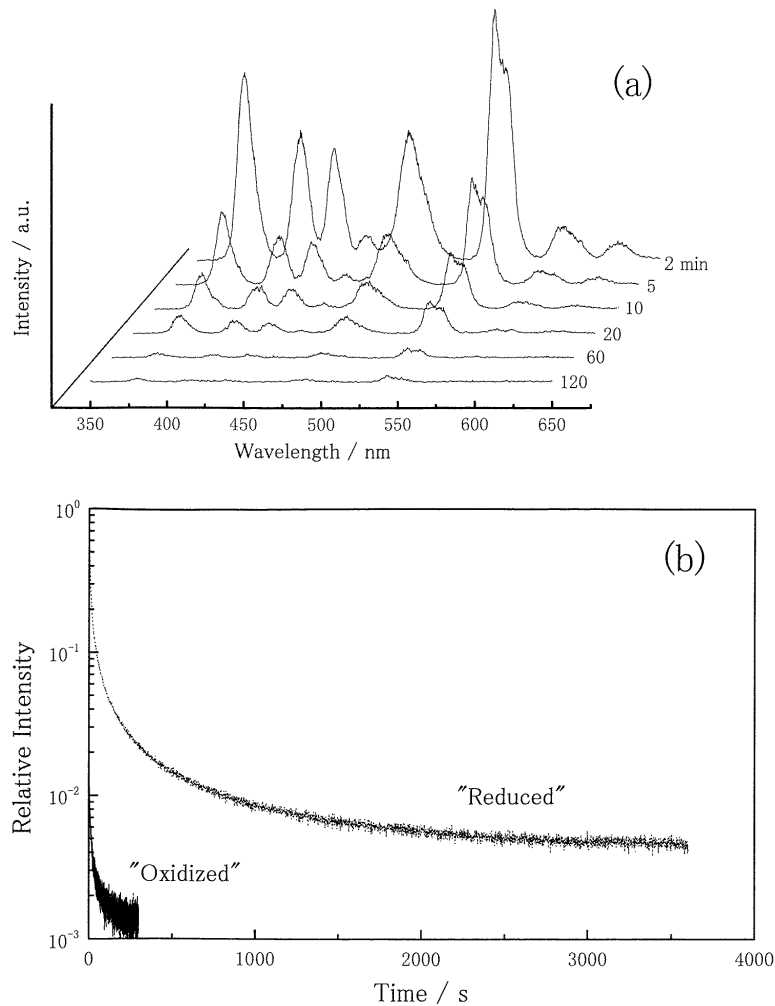


Figure 2. (a) Change in photoluminescence spectra of the ‘reduced’ glasses with the duration after stopping 10 min exposure to 254 nm light of a conventional fluorescence spectrometer. Excitation: 250 nm. The spectrometer sensitivity remains constant for all the spectra. The speed of wavelength scanning was 1200 nm min^{-1} . Intensity correction of phosphorescence at each wavelength due to the difference in time delay after interruption of uv illumination was not made. (b) Intensity decay of the photoluminescence, monitored at the wavelength of 543 nm, after stopping 10 min exposure to 254 nm light of a conventional fluorescence spectrometer. The conditions of light illumination and the spectrometric measurements are the same for the oxidized and reduced glasses.

of Tb^{4+} in ThO_2 and BaZrO_3 [10]. The ‘oxidized’ glasses are very oxidizing hosts because they contain a considerable amount of chemically dissolved O_2 species such as peroxylinkages and superoxide radical ions and physically dissolved O_2 molecules [3, 4]. Thus, the additional absorption band around $\sim 350 \text{ nm}$ is attributed to the charge transfer transition (oxygen $\rightarrow \text{Tb}^{4+}$). Figure 1(b) shows photoluminescence and photoexcitation spectra of the glasses. No qualitative difference was noted between the ‘oxidized’ and ‘reduced’ glasses. The luminescence spectrum upon excitation with 254 nm light is a

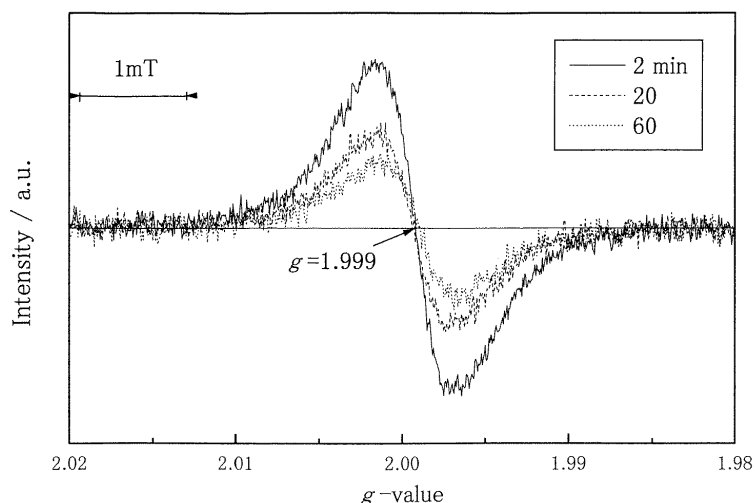


Figure 3. Light-induced EPR signals in reduced calcium aluminate glasses doped with Tb ions and their change after stopping the illumination. The specimen in the microwave cavity was illuminated with 254 nm light from an Hg/Xe lamp through an optical window. Light illumination and EPR measurements were made at ~ 300 K.

typical pattern of the emission from Tb³⁺, i.e., the two series of emission lines arising from $^5D_4 \rightarrow ^7F_{J'}$ ($J' = 6-0$) and $^5D_3 \rightarrow ^7F_{J'}$ ($J' = 6-1$) transitions are seen in the wavelength regions of 480–700 nm and 380–470 nm, respectively. The excitation band for the $^5D_4 \rightarrow ^7F_5$ emission (543 nm) is located around 250 nm. This band corresponds to the absorption band due to a d–f transition ($4f^8 \rightarrow 4f^7 5d^1$) of Tb³⁺ ions.

Figure 2(a) shows a series of photoluminescence spectra of the ‘reduced’ glasses after interruption of 254 nm light illumination. The phosphorescence is observable even after 120 min and no change in the spectral shape occurs during the whole decay processes up to 2 h. It is therefore evident that the ‘reduced’ glasses have long lasting phosphorescence properties arising from Tb³⁺ ions. Figure 2(b) shows the intensity decay of the phosphorescence monitored at the peak position (543 nm) of the $^5D_4 \rightarrow ^7F_5$ transition. The phosphorescence intensity in the ‘reduced’ glasses is higher by two orders of magnitude than that in the ‘oxidized’ glasses. The curves do not obey a simple exponential decay, indicating that the relaxation time is not a constant but has a statistical distribution.

When the ‘reduced’ glasses are illuminated with 254 nm light, an EPR signal shown in figure 3 is induced. The signal has an almost symmetric shape, a full width at half maximum of 0.85 mT and a g -value of 1.999. These features agree well with those of an electron trapped at the oxygen vacancy site surrounded by Ca²⁺ ions (the naturally abundant Ca nuclei have no nuclear magnetic moment) reported in the Tb-free, ‘reduced’ calcium aluminate glasses [8]. Thus, this induced signal is ascribed to an electron trapped at the site of an oxygen vacancy surrounded by Ca²⁺ ions, i.e., an F⁺-like centre in CaO. The intensities of this EPR signal decay with time after the interruption of uv illumination as shown in the figure. The aluminum–oxygen hole centre, which gives a hyperfine structure due to the ²⁷Al nucleus (abundance = 100%, nuclear spin = 5/2), should appear [3] if a positive hole generated by photo-excitation is trapped on an oxygen connected with an Al³⁺ ion in the Tb-free calcium aluminate glasses. However, no EPR signal was induced except the signal at $g = 1.999$.

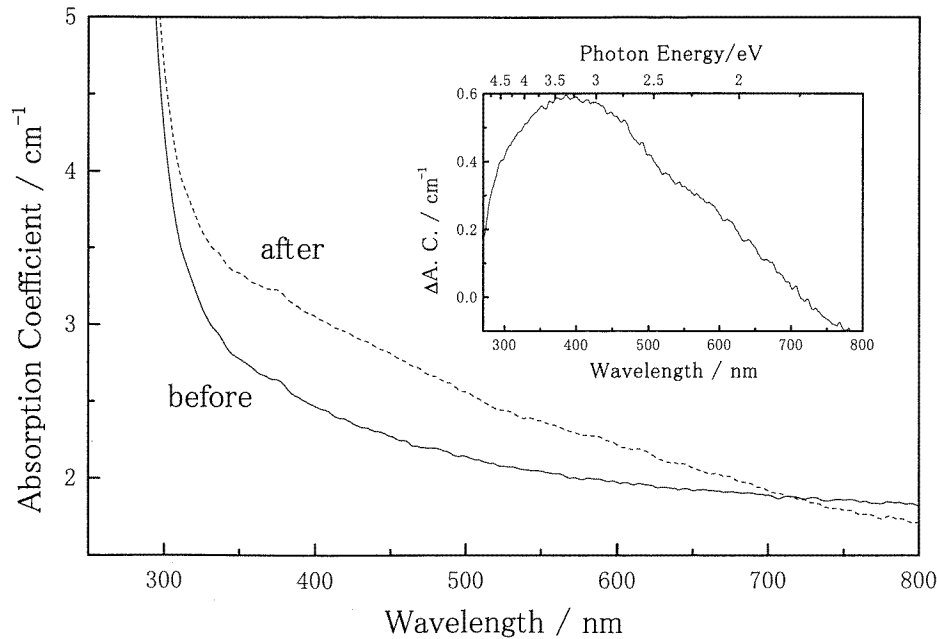
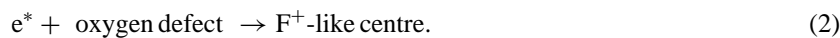


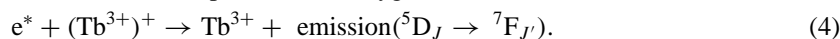
Figure 4. Change in optical absorption spectra of reduced calcium aluminate glasses doped with Tb ions with light illumination. —: before uv illumination, - - -: after uv illumination for 15 min. Light: 254 nm (intensity 1.7 mW cm^{-2}) from filtered Xe/Hg lamp. Inset shows effectively induced absorption spectrum, which was obtained by subtracting the spectrum of the specimen before illumination from that after illumination. The induced absorption is composed of the main band peaking around 350 nm and a shoulder around 600 nm. The former and the latter bands are ascribed to the charge transfer transition of Tb^{4+} ions and the absorption of F^+ -like centres [8], respectively.

Figure 4 shows the optical absorption spectra of the ‘reduced’ glasses (Tb-doped) before and after 254 nm light illumination. The inset is the absorption effectively induced by the illumination. The induced absorption is broad (extending from $<280 \text{ nm}$ to $>600 \text{ nm}$) and has peaks around 350 nm and 600 nm. The position of the former band is close to that of the charge transfer band of Tb^{4+} ions in the ‘oxidized’ glasses (figure 1(a)). The latter band agrees with that of the F^+ -like centre in Tb-free reduced calcium aluminate glasses [8]. It is therefore concluded that uv illumination leading to a long lasting phosphorescence induces photo-oxidation of Tb^{3+} in the ‘reduced’ glasses.

The experimental results described above are consistent with our idea of realizing a long lasting phosphorescent glass, i.e., a combination of a valence-alternative phosphor ion with an oxygen vacancy which may form a metastable centre by capturing an electron generated by photoexcitation leads to emergence of long lasting phosphorescence. The following mechanism is suggested for the present glasses. During uv illumination



After illumination



Here, a photo-oxidized Tb³⁺ is denoted as (Tb³⁺)⁺ to discriminate from a Tb⁴⁺ produced by thermal processes. The oxygen vacancy and e* denote an oxygen vacancy surrounded by Ca²⁺ ions and an excited electron, respectively. The photo-oxidized Tb³⁺, (Tb³⁺)⁺, is metastable compared with thermally created Tb⁴⁺ observed in the 'oxidized' glasses because a local structural rearrangement followed by photo-oxidation is not expected in the rigid state near room temperature. The potential barrier height for electron trapping in the F⁺-like centre in the 'reduced' glasses is comparable to the thermal energy (~25 meV) around room temperature as evidenced by the fact that the F⁺-like centre is the origin of phototropy in the reduced calcium aluminate glasses (Tb free). Thus, (Tb³⁺)⁺ and the F⁺-like centre may be regarded as a high energy state created by light illumination. This state is relaxed by emission of photoluminescence from an excited state of Tb³⁺ ions via recombination of an electron thermally released from the F⁺-like centre with a (Tb³⁺)⁺ ion. A detailed study on the mechanism including the analysis of decay behaviour of intensities of the phosphorescence and the uv-induced EPR signal is in progress along with efforts to improve long lasting phosphorescence properties.

Note added in proof. We received a reprint of a paper by J Qiu and K Hirao (1998 *Solid State Commun.* **106** 795) reporting long lasting luminescence (LLL) in Eu²⁺-doped CaO-Al₂O₃-B₂O₃ glasses after submission of this paper. The authors suggest the important role of oxygen vacancies as an electron trap in the emergence of the LLL.

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