Preparation and optical properties of CeF$_3$-containing oxide fluoride glasses

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ABSTRACT

Cerium-containing oxide fluoride glasses CeF$_3$–BaF$_2$–AlF$_3$–SiO$_2$ were prepared under CO and Ar atmospheres. The glass prepared in a CO atmosphere exhibited blue emission under UV irradiation because the hydrolysis of CeF$_3$ to a Ce^{4+}-containing compound during heating process was controlled. The emission spectrum was separable into three peak components by peak analysis. X-ray photoelectron spectroscopy (XPS) spectra were measured to investigate the valency of the elements in the glass. Oxide and fluoride ions in the glass respectively have different electronic states from those in CeO$_2$ and CeF$_3$. The electronic state of cerium ion in the oxide fluoride glass differed from that in CeO$_2$ and CeF$_3$.

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1. Introduction

We had previously reported the preparation and properties of oxide fluoride glasses containing rare earth elements [1–3]. The oxide fluoride glasses are anticipated for use as a new optical material. Every rare earth element has the emission spectrum of a specific wavelength because of its configuration of electrons in 4f orbitals. Cerium is the most common among rare earth elements in the earth's crust: approximately 40% of rare earth elements [4] and Ce^{3+} are considered as key elements for use in optical devices [5–9]. Studies investigating cerium compounds for their use in catalysts, abrasive materials, solid electrolytes, and optical materials are also widely reported [10]. In those studies, the control of the valence of cerium ion is important to control the optical properties of the glasses. Especially, the Ce^{3+} content is related directly to the performance of the compounds as scintillation counter materials, phosphors, and LED materials [8,11–13]. Radiation emission of Ce^{3+} causes the transitions between the 4f and 5d electronic states. The 5d electronic state is influenced by the ligand field. An approach combining the anions (O^{2-} and Cl$^-$) is sometimes used for improvement of the light yield [12]. From this perspective, oxide fluoride glasses that contain two different anions might also be interesting for study because fluoride ions have very close ionic

radius to O^{2-} and lower polarizability. Although many reports related to oxide or fluoride glass describe their structure and properties, oxide fluoride glasses have not been studied because of the difficulty of their preparation. It is difficult to prepare oxide fluoride glasses containing lanthanide ions because of hydrolysis of lanthanide trifluorides during melting processes. For example, CeF$_3$ is useful as a dopant for oxide glasses [7] but it is difficult to avoid hydrolysis of CeF$_3$ (dried to the greatest extent possible under vacuum) during melting process, even in Ar atmosphere containing 10 ppm H$_2$O. As described in an earlier study [7], fluorine must be lost during the melting process because the melting temperature was more than 1000 °C [14]. Consequently, the product was not an oxide fluoride glass, but rather an oxide glass because the hydrolysis of CeF$_3$ occurs at temperatures greater than 700 °C, as described above. This hydrolysis of CeF$_3$ and the subsequent oxidation of Ce^{3+} generate Ce^{4+} in the product.

Among oxide fluoride glasses containing rare earth elements, CeF$_3$–BaF$_2$–AlF$_3$–SiO$_2$ glasses were investigated in this study. The glasses in this system were brown when they were produced, even when produced in inert gas (Ar). The brown color is attributable to the presence of both Ce^{3+} and Ce^{4+} ions that have different energy levels in the glass. The energy transition which takes place between Ce^{3+} and Ce^{4+} causes the brown color. This mixed-valence state of cerium ion resulted from hydrolysis and oxidation at a high temperature. This report is the first describing that colorless or light yellow CeF$_3$–BaF$_2$–AlF$_3$–SiO$_2$ glass was obtained instead of brown glass when the glass was produced in a CO atmosphere.

Table 1
Analysis of emission spectra of $10CeF_3–20BaF_2–10AlF_3–60SiO_2$ glass using a Gaussian function for several excitation wavelengths

λ_{Ex}	Peak 1			Peak 2			Peak 3		
	Amplitude	Center wavelength (nm)	FHWM	Amplitude	Center wavelength (nm)	FHWM	Amplitude	Center wavelength (nm)	FHWM
310	27.94	410.34 ± 0.78	49.18	61.33	446.03 ± 3.29	77.30	26.93	499.00 ± 19.08	122.98
320	28.92	410.93 ± 0.67	49.57	62.66	447.12 ± 3.57	79.97	25.07	500.51 ± 19.01	130.60
330	25.39	411.61 ± 0.78	48.12	60.24	445.71 ± 3.98	77.01	27.65	495.07 ± 23.74	121.49
357	16.78	413.90 ± 0.27	42.50	60.32	442.86 ± 3.41	76.19	33.05	486.55 ± 17.37	126.22
366	12.32	418.68 ± 0.27	32.49	52.77	445.26 ± 1.35	73.34	43.40	473.75 ± 2.75	138.96

Cerium ion oxidization is controlled in this case. The amount of Ce^{3+} in the glass increased and a very low Ce^{4+} content was achieved. These glasses have blue emissions from Ce^{3+} under UV irradiation (365 nm). Although it has been reported that the addition of carbon powder during melting is effective to avert the oxidation of Ce^{3+} to Ce^{4+} in case of oxide glasses, the decomposition and/or hydrolysis of CeF_3 was not averted in the case of oxide fluoride glasses. In addition, the Pt or Pt/Au container was badly damaged when using a H_2 atmosphere. In this work, glasses having different characteristics can be prepared under an Ar or CO atmosphere.

2. Results and discussion

2.1. Preparation of oxide fluoride glasses containing CeF_3

Pale yellow glasses were obtained in $CeF_3–BaF_2–AlF_3–SiO_2$ system in A CO atmosphere. At the composition around $10CeF_3–20BaF_2–10AlF_3–60SiO_2$ or $20CeF_3–10BaF_2–10AlF_3–60SiO_2$, the glass was prepared reproducibly by heating to 1300 °C for 90 min. By optimizing the conditions such as heating temperature, holding time, heating rate, and controlling the hydrolysis of rare earth fluoride, the composition range to prepare the glass was extended slightly. Brown glass tended to be obtained in cases of higher CeF_3 contents, even in CO. It was possible to produce a glass containing 40 mol% of CeF_3 as a maximum. Fig. 1 depicts the glass forming composition of $CeF_3–BaF_2–AlF_3–SiO_2$ glass. The open circle shows a composition with which the glass formation was possible by heating at 1300 °C, with 30–90 min holding. The closed circle signifies a composition with which the glass formation was not possible. During the glass preparation process, the sample weight decreased by about 18 wt%. Fluorine must be lost completely if this weight loss resulted from the hydrolysis only. However, X-ray

fluorescent spectroscopy (XFS) measurements confirmed that 43% and 22% of fluorine in the starting mixture remained in the product prepared respectively in CO and Ar atmospheres. Therefore, the CeF_3 hydrolysis was controlled in a CO atmosphere, although CeF_3 was hydrolyzed during preparation process in CO and Ar atmospheres. The hydrolysis of LnF_3 proceeds to produce Ln_2O_3 via LnO_xF_y [14]. For cerium, the final product of hydrolysis is CeO_2, which might be derived from Ce_2O_3 and/or CeO_xF_y: the hydrolysis of CeF_3 includes several reaction processes. For the glasses described here, the reaction from CeO_xF_y to CeO_2 seems to be controlled in a CO atmosphere. For melting in an Ar atmosphere, the oxidative decomposition of CeO_xF_y (the reaction with H_2O and O_2 to produce HF) proceeds and Ce^{4+} generates in the sample (x value increases). The total reaction from CeF_3 to CeO_2 might be the following equation: $2CeF_3 + 3H_2O + 1/2O_2 = 2CeO_2 + 6HF$. The O_2 which contaminates the atmosphere used for production might be an oxidizer in this case. Furthermore, CO might greatly reduce the partial pressure of O_2 in the atmosphere by $CO + 1/2O_2 = CO_2$ equilibrium.

2.2. Fluorescence spectra of the CeF_3-containing oxide fluoride glasses produced in a CO atmosphere

The brown $Ce^{3+}–Ce^{4+}$ oxide fluoride glass produced in Ar atmosphere emitted no fluorescence, although the glass produced in CO gas exhibited blue emission under UV irradiation (365 nm). Fig. 2 depicts profiles of the excitation spectra under emission wavelength at 435 nm. Two broad peaks are observed at 320 and 348 nm in the excitation spectra. The peak at 320 nm was larger than that at 348 nm. Therefore, the wavelength for the excitation of the emission spectra was determined as 320 nm for $10CeF_3–20BaF_2–10AlF_3–60SiO_2$ glasses. Fig. 3 depicts profiles of the emission spectra excited at 310, 320, 330, 357, and 366 nm. Radiation absorption and emission of Ce^{3+} occur because of the transition of an electron from the 4f orbital into the 5d orbital [15].
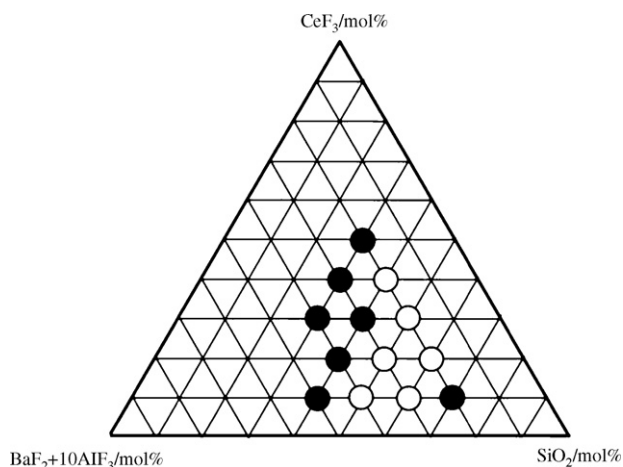
Fig. 1. Glass forming composition of $CeF_3–BaF_2–10AlF_3–SiO_2$ system by nominal composition. Open circles indicate that the glass was producible. Closed circles indicate that the glass was not producible.
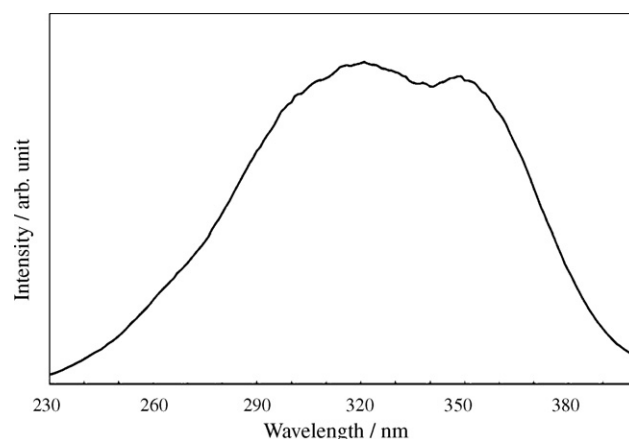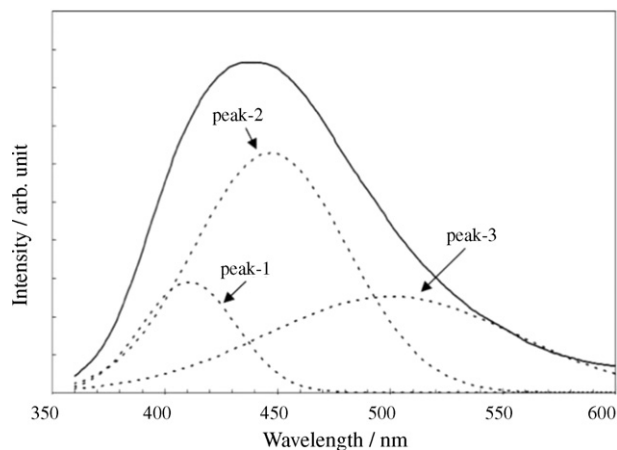

Fig. 2. Excitation spectrum of $10CeF_3–20BaF_2–10AlF_3–60SiO_2$ glass prepared in CO. The excitation spectrum under the emission wavelength at 435 nm.
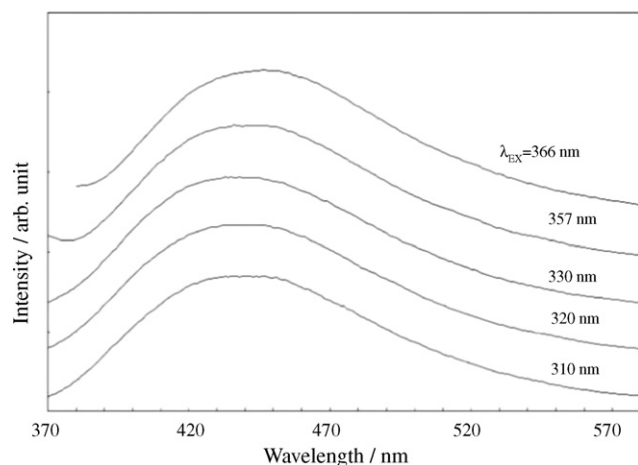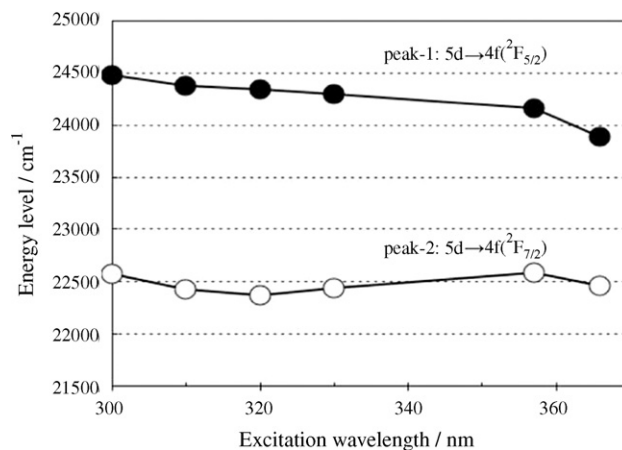
Fig. 3. Emission spectra of $10CeF_3–20BaF_2–10AlF_3–60SiO_2$ glass prepared in CO for several excitation wavelengths.

Fig. 5. Energy differences of peaks 1 and 2 for several excitation wavelengths of $10CeF_3–20BaF_2–10AlF_3–60SiO_2$ glass prepared in CO.

Generally, the profile in the emission spectra corresponding to the 4f–5d transition is broader than the 4f–4f transition. As depicted in Fig. 3, the peak position for excitation at 320 nm was of a shorter wavelength than that at 357 nm excitation. The peak was deconvoluted using a Gaussian function to investigate these differences in the emission profiles in detail. Fig. 4 depicts the result of the peak analysis of the emission profile excited at 320 nm. Results for all profiles portrayed in Fig. 3 are presented in Table 1. Every emission peak consisted of three peaks of about 410 (peak 1), 445 (peak 2), and 490 nm (peak 3). Matsui et al. [16] also reported the existence of three peaks from peak analysis of the Ce^{3+} emission spectrum in $Y_2SiO_5:Ce^{3+}$ crystal. The difference between peaks 1 and 2 might correspond to the split (2000 cm^{-1}) of $^2F_{5/2}$ and $^2F_{7/2}$ by spin–orbit interaction [15–20]. Peak 3 corresponds to the presence of Ce^{3+} with CN = 7, whereas peaks 1 and 2 correspond to that with CN = 6 reported in the literature. Therefore, Ce^{3+} of two kinds might be located in different environments in the glass considered here. Peak analysis results show that the intensity of peak 3 tends to be stronger when the excitation wavelength is elongated. The quantum efficiency for peak 3 might depend on the environment around Ce^{3+}. Fig. 5 depicts the energy calculated from each wavelength of peaks 1 and 2. The energy differences between peaks 1 and 2 are approximately 1600 cm^{-1}; they became small in relation to the energy difference of $^2F_{5/2}$, and

$^2F_{7/2}$. As reported by Matsui et al., the presence of two kinds of Ce^{3+} cations in $Y_2SiO_5:Ce^{3+}$ seems to cause too small of an energy difference between the $^2F_{5/2}$ and $^2F_{7/2}$ levels [16]. The results in Fig. 5 might be consistent with that presupposition. It is inferred that some variation in the environment around Ce^{3+} exists in the glasses described here.

2.3. X-ray photoelectron spectroscopy (XPS) spectra of CeF_3-containing oxide fluoride glasses

Figs. 6–9 portray XPS spectra of F 1s, O 1s, Ce 3d, and Ce 4d in glasses prepared in an Ar and a CO atmospheres. The F 1s peak in the glass prepared in a CO atmosphere was more intense than that in the glass prepared in an Ar atmosphere, as presented in Fig. 6; furthermore, the peak position shifted to a lower energy than that of CeF_3. Consequently, there is less fluoride ion in the glass prepared in an Ar atmosphere than in the glass prepared in a CO atmosphere. This difference is consistent with the result of quantitative analysis of fluoride ion by XFS measurement

Fig. 4. Decomposition of the emission spectrum of $10CeF_3–20BaF_2–10AlF_3–60SiO_2$ glass prepared in CO under the excitation wavelength at 320 nm. The solid line shows the observed spectrum. The dashed lines show calculated spectra.
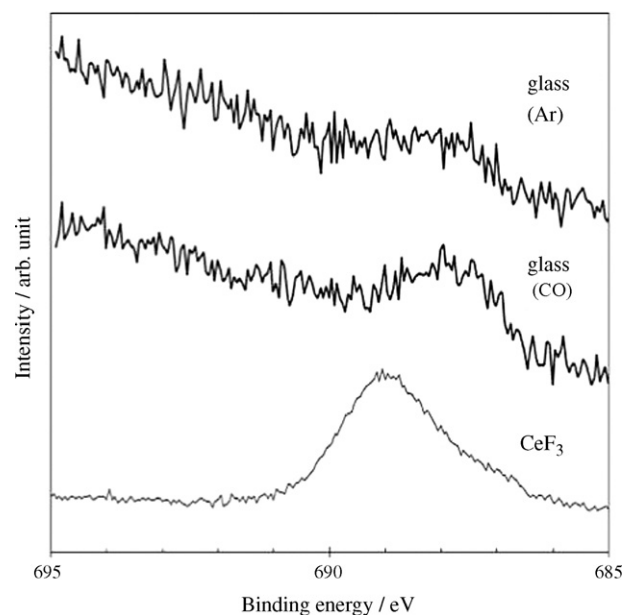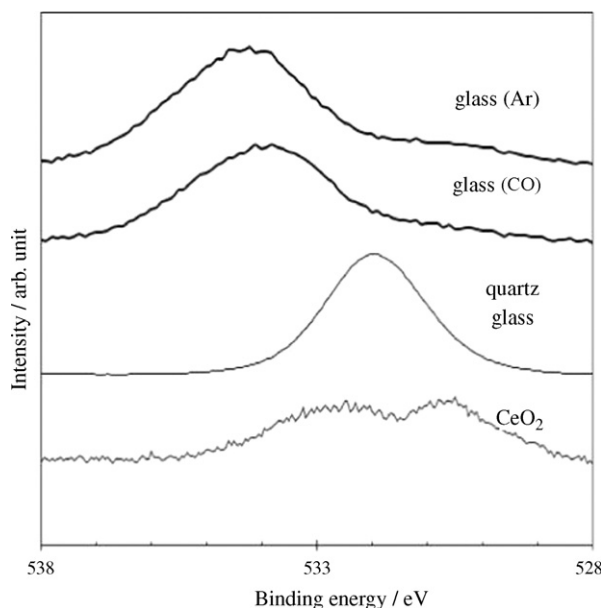

Fig. 6. F 1s spectra of CeF_3 and $10CeF_3–20BaF_2–10AlF_3–60SiO_2$ glasses prepared in a CO and an Ar atmospheres.

Fig. 7. O 1s spectra of CeO_2, quartz glass and $10CeF_3$–$20BaF_2$–$10AlF_3$–$60SiO_2$ glasses prepared in CO and Ar atmospheres.

Fig. 9. Ce 4d spectra of CeF_3, CeO_2 and $10CeF_3$–$20BaF_2$–$10AlF_3$–$60SiO_2$ glasses prepared in Ar and CO atmospheres.

described previously. The oxidative decomposition of the Ce^{3+}-containing intermediate (CeO_xF_y where $2x + y = 3$) such as CeOF generated by hydrolysis of CeF_3 was apparently controlled in a CO atmosphere. The fluoride ion withdraws the electron cloud more strongly than oxide ion. Therefore, the electron cloud seems to be withdrawn to fluoride ion in CeO_xF_y ($2x + y = 3$) more than in CeF_3. This withdrawal causes the smaller binding energy of F 1s electron of the oxide fluoride glass than that of CeF_3. A single peak existed in XPS spectra of O 1s in the glasses prepared here, although a double peak was observed in that in CeO_2. The peak position for the glasses prepared in a CO or an Ar atmosphere was higher than that for the quartz glass because the electron density around O^{2-} might have been lowered: the electron cloud is withdrawn toward F^- via cerium ion. The oxide and fluoride ions in the glass respectively have different electronic states from those in simple oxide and

fluoride. The Ce 3d and Ce 4d spectra are shown in Figs. 8 and 9 to elucidate the state of the valence of cerium in the glasses. The CeF_3 and CeO_2 were measured respectively as the references for Ce^{3+} and Ce^{4+}. The peak profiles for Ce 3d and Ce 4d electrons in the glasses prepared in CO and Ar atmospheres were mutually similar. However, differences in peak positions were apparent. Figs. 8 and 9 show that the peaks of the glass prepared in a CO atmosphere had lower binding energy (about 0.3 eV) than those in an Ar atmosphere. The peak position and profile in XPS spectra depend on the valence state. The mean valence of cerium ion increases when the oxidative decomposition of CeO_xF_y proceeds. The ratio of Ce^{3+}/Ce^{4+} of the glasses prepared in a CO atmosphere was larger than those prepared in an Ar atmosphere. Therefore, the peaks in the XPS spectra of the glasses prepared in a CO atmosphere must locate at a lower binding energy than the glasses prepared in an Ar atmosphere. In fact, this difference was observed in Figs. 8 and 9. In Ce 3d spectra, the peak at 919 eV that appeared in the spectrum of CeO_2 was not observed in that of the glasses (Fig. 8). Furthermore, the peak pattern of the glasses in Fig. 8 differed completely from that of CeF_3 [21–23]. Fig. 9 presents the Ce 4d spectra of both glasses. The peak near 105 eV corresponds to Si 2p. The peaks at 109 eV (not identified yet), 123 eV ($4d_{5/2}$), and 126 eV ($4d_{3/2}$) that appeared in the spectrum of CeO_2 were not observed in the glasses' spectra (Fig. 9). The peak pattern of the glasses in Fig. 9 differed completely from that of CeF_3. The electronic state of cerium ion must be distinctive to the glass obtained in this study. In other words, the presence of both fluoride and oxide ions might impart a unique electronic state to cerium.

3. Conclusion

Pale yellow glasses were obtained in the CeF_3–BaF_2–AlF_3–SiO_2 system in CO. At compositions around $10CeF_3$–$20BaF_2$–$10AlF_3$–$60SiO_2$ and $20CeF_3$–$10BaF_2$–$10AlF_3$–$60SiO_2$, glasses were prepared reproducibly at 1300 °C heating, with 90 min holding. It was possible to prepare glass containing 40 mol% of CeF_3, which is the maximum attempted in this study. The CeF_3-containing oxide fluoride glass prepared in CO exhibited blue emission under UV irradiation. The emission spectrum was separable into three peaks with peak positions at about at 410 (peak 1), 445 (peak 2), and

Fig. 8. Ce 3d spectra of CeF_3, CeO_2 and $10CeF_3$–$20BaF_2$–$10AlF_3$–$60SiO_2$ glasses prepared in Ar and CO atmospheres.

490 nm (peak 3). The energy difference between peaks 1 and 2 might correspond to the split of $^2F_{5/2}$ and $^2F_{7/2}$ by spin–orbit interaction. The intensity of peak 3 tends to be larger when the excitation wavelength lengthens. Two kinds of Ce^{3+} might be located in different environments in the glasses. Results from XPS measurements show that the oxide and fluoride ions in the glass prepared in this study respectively have different electronic states from those in simple oxide and fluoride. The peak profiles for Ce 3d and Ce 4d electrons in the glasses prepared in a CO and an Ar were mutually similar, but differed completely from those of CeF_3 and CeO_2. The differences in the peak positions were of about 0.3 eV. These results suggest that the presence of both fluoride and oxide ions might impart an electronic state to cerium ion in the oxide fluoride glass that differs from that in CeF_3 or CeO_2. The change in the mean valence of cerium ion might be reflected in the difference in the peak position.

4. Experimental

The starting materials used for this study were CeF_3 (4N; Soekawa Chemical Co. Ltd.), BaF_2 (4N; Soekawa Chemical Co. Ltd.), AlF_3 (3N; Wako Pure Chemical Industries Ltd.), and SiO_2 (3N; Kishida Chemical Co. Ltd.). Those starting materials were mixed using an alumina mortar. The mixture was dried under vacuum for more than 12 h. The mixture was then compressed in a platinum boat and set in an electric furnace filled with CO or Ar gas. The mixture was heated to 1300 °C at 7–10 °C min^{-1} and held for 30–90 min. For quenching, it was taken out from the furnace and was then put onto a molecular sieve (Molecular Sieves 13× 1/8; Wako Pure Chemical Industries Ltd.) bed cooled with liquid nitrogen. The cooling rate was ca. 130 °C s^{-1}. For each glass composition, the maximum temperature was fixed and optimization of the heating rate and holding time were attempted.

The products were characterized using X-ray powder diffraction (XRD, RINT2100; Rigaku Corp.). The fluorescence of the product was confirmed using a UV light (365 nm wavelength). The fluorescence spectrum was measured using a spectrophotometer (Spectrophotometer 850; Hitachi Ltd.). After the obtained peaks of fluorescence spectra were analyzed and separated using peak analysis software (PeakFit; SeaSolve Software Inc.), the electronic states of the elements in the glass were assessed using X-ray photoelectron spectroscopy (XPS, JPS-9010MC; JEOL).

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