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メタデータ	言語: English 出版者: 公開日: 2009-05-08 キーワード (Ja): キーワード (En): 作成者: TAKAHASHI, Hirosh, YONEZAWA, Susumu, KAWAI, Masayuk, TAKASHIMA, Masayuki メールアドレス: 所属:
URL	http://hdl.handle.net/10098/2037

Preparation and optical properties of CeF_3 containing oxide fluoride glasses

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Keyword; Oxide fluoride glass; Cerium fluoride; CO atmosphere; Luminescence; X-ray photoelectron spectroscopy (XPS)

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 CO exhibited blue emission under UV irradiation. Peak analyzes were performed to investigate their optical properties. The emission spectra were separable into three peak components by peak analysis. X-ray photoemission spectroscopy (XPS) spectra were measured to investigate the valency of the elements in the glass. Oxygen and fluorine in the glasses were more covalent and ionic than those in simple oxide and fluoride compounds. The cerium ion in the glass prepared in CO might be under a cationic condition whereas that in Ar might be under an anionic condition.

1. Introduction

We have reported the preparation and properties of oxide fluoride glasses containing rare earth elements [1–3]. The oxide fluoride glasses were anticipated as a new optical material that has functions of both oxide and fluoride glasses. Every rare earth element has unique optical properties because of its arrangement of electrons in the 4f orbital. Cerium is the most common among rare earth elements in the earth's crust: about 40% [4] and Ce^{3+} is attracted as the key element for optical devices [5-9]. Studies investigating cerium compounds for their use in catalysts, abrasive materials, solid electrolytes, and optical materials, etc. are also widely done [10]. In those researches it has been reported the control of the valence of cerium ion is important. Especially the content of Ce^{3+} must directly reflect to the performance of the compound as the scintillation counter material, phosphor and LED materials [8, 11-13]. Radiation of Ce^{3+} is causes due to transitions between the 4f and 5d electronic states. The 5d electronic state is influenced to the ligand field. There is approach of combining the anion (using Cl^-) for improve the light yield [12]. In this point of view, oxide fluoride glasses which contains two different anions may also be interesting to be studied. The properties of oxide fluoride glasses have not been summarized systematically yet, as they have been for oxide or fluoride glasses. This is because the oxide fluoride glasses containing large amount of lanthanide trifluorides is greatly affected by their hydrolysis during melting process. For example, CeF_3 can be used as the dopant for the oxide glass [7]. But it must be difficult to avid to undergo the hydrolysis of CeF_3. In case of Ref.[7], fluorine must be lost during melting process because the melting temperature was more than 1000°C [14]. That means the product was not an oxide fluoride glass but an oxide glass. This hydrolysis of CeF_3 causes the generation of Ce^{4+} in the product.

Among oxide fluoride glasses containing the 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 in inert gas (Ar). The brown color is attributable to the presence of two ions—Ce^{3+} and Ce^{4+}—which have different energy levels in the glass. The energy transitions might take place between Ce^{3+} and Ce^{4+} to be brown. Mixed valency of cerium ion resulted from hydrolysis at high temperature. Furthermore, CeF_3 has unique behavior of hydrolysis at 500°C among the rare earth elements [14]. It was first found in this paper that colorless or light yellow glass was obtained instead of brown glass when these glasses were produced in a CO atmosphere. Oxidization of cerium ion is controlled in this case. The amount of Ce^{3+} in the glass increased and very low content of Ce^{4+} was achieved. These glasses have blue emission from Ce^{3+} under UV irradiation (365 nm). Although it has been reported that the addition of carbon powder during melting is effective to avoid the oxidation of Ce^{3+} to Ce^{4+} in case of oxide glasses, the decomposition and/of hydrolysis of CeF_3 was not avoided in case of the oxide fluoride glasses. In addition, the Pt or Pt/Au container was badly damaged in case of using H_2 atmosphere. In this work, the 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 CO. 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 at 1300°C heating, with 90 min holding. Optimizing the conditions such as heating temperature, hold time, heating rate, and controlling the hydrolysis of rare earth fluoride, the composition range to prepare the glass was slightly enlarged. Brown glass tended to be obtained in cases of higher CeF_3 contents, even in CO. It was possible to produce a glass containing a maximum of 40 mol% of CeF_3. Fig. 1 depicts the phase diagram of CeF_3-BaF_2-AlF_3-SiO_2 glass. The open circle shows a composition with which the glass formation was possible by firing at 1300°C, with 30–90 min holding. The closed circle shows a composition with which the glass formation was not possible.

At temperatures higher than 500°C, $CeF_3(Ce^{3+})$ can be hydrolyzed to form $CeO_2(Ce^{4+})$

[14]. The brown color is inferred to be caused by mixing Ce^{3+} and Ce^{4+} in the sample. In a CO atmosphere, oxidization of Ce^{3+} in CeF_3 can be prevented. Although reduction firing using H_2 was also examined, the platinum boat deteriorated and no glass was obtained.

2-2. Fluorescence spectra of the CeF_3-containing oxide fluoride glasses produced in CO atmosphere

The CeF_3-containing oxide fluoride glass produced in an Ar atmosphere which was brown didn't emit any fluorescence, while the glass produced in CO gas exhibited blue emission under UV irradiation (365 nm). Fig. 2 depicts the profiles of the excitation spectra under emission wavelength at 435. Two peaks are shown at 320 nm and 348 nm in the excitation spectra. The peak at 320 nm was larger than that at 348 nm. Therefore, the wavelength of the excitation for the emission spectra was determined as 320 nm spectra of $10CeF_3$-$20BaF_2$-$10AlF_3$-$60SiO_2$ glasses. Fig. 3 depicts the profiles of the emission spectra excited at 310, 320, 330, 357 and 366 nm. Absorption and radiation of Ce^{3+} occur because of the transition of an electron from the 4f orbital into the 5d orbital [15]. Generally, the profile in the emission spectra corresponds to the 4f-5d transition, which is broader than the 4f-4f transition. As shown in Fig. 3, the peak position for excitation at 320 nm was located at a shorter wavelength rather than that at 357 nm. To investigate these differences in the emission profiles in detail, the peak was deconvoluted using a Gaussian function. Fig. 4 depicts the result of the peak analysis of the emission profile excited at 320 nm. The results for all profiles portrayed in Fig. 3 are presented in Table 1. Every emission peak consisted of three peaks that have the peak position at about 410 (peak-1), 445 (peak-2), and 490 nm (peak-3). Matsui et al. [16] also reported the existence of the three peaks from peak analysis of the emission spectrum according to a Ce^{3+} in Y_2SiO_5 crystal. The difference between peak-1 and peak-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 peak-1 and peak-2 corresponds to that with CN=6 reported in the literature. Therefore, two kinds of Ce^{3+} might be located in different environments in the glass in this study.

As a result of peak analysis, the intensity of peak-3 tends to be strong when the excitation wavelength lengthens. The quantum efficiency for peak-3 might depend on the environment around the Ce^{3+}. Fig. 5 depicts the energy calculated from each wavelength of peak-1 and the peak-2. The energy differences between peak-1 and peak-2 are about 1600 cm^{-1}; they became small compared 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+} doped in Y_2SiO_5 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 supposition. There must be variation in the environment around Ce^{3+} in the glasses here.

2-3. XPS (X-ray photoelectron spectroscopy) spectra of the CeF_3-containing oxide fluoride glasses

Figures 6–9 show XPS spectra of F1s, O1s, Ce3d, and Ce4d in glasses prepared in Ar and CO. The peak for F1s in the glass prepared in CO was larger than that in Ar, as presented in Fig. 6. The peak position was shifted to a lower energy than that of CeF_3. Therefore, there is less fluoride ion in the glass prepared in Ar than that prepared in CO. This difference according to glass production atmospheres probably results from hydrolysis during the firing process. The hydrolysis of CeF_3 involved the oxidation reaction from Ce^{3+} to Ce^{4+}. Consequently, the hydrolysis reaction was inhibited by a controlled oxidation reaction in the presence of CO. A single peak existed in XPS spectra of O1s in the glasses prepared here, although a double peak was observed in that in CeO_2. The peak position for the glasses prepared in CO or Ar was higher than that for the quartz glass. Consequently, oxygen and fluorine in the glasses prepared in this study were respectively more covalent and ionic than those in simple oxide and fluoride compounds. To elucidate the state of the valence of cerium in the glasses, Ce3d and Ce4d spectra are shown in Figs. 8 and 9. In addition, CeF_3 and CeO_2 were measured respectively as the references for Ce^{3+} and Ce^{4+}. The peak profiles for Ce3d and Ce4d electrons in the glasses prepared in CO and Ar were mutually similar. In Ce3d 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: the peak pattern for Ce3d electron in the glasses must be distinctive to the glass [21–23]. No difference in the peak patterns of the glasses prepared in CO and Ar shown in Fig. 8 was observed, even though the difference in the valence states of the cerium ion in both glasses was clearly distinguishable by their color and fluorescence characteristics. Generally, the peak position and/or profile in XPS spectra depend on the valence state. In this case, the change in the valence state of cerium ions in the glasses might be compensated by the balance of the anion composition, e.g., the contents of oxide and fluoride ions. As already described, the peak of F1s electron in the glass was shifted to the low energy direction; the peak of O1s electron is shifted to the higher energy direction (Figs. 6 and 7). In addition, the fluoride ion content in the glass prepared in CO was higher than that in Ar. From these results, the cerium ions in the glasses prepared in CO are inferred to be surrounded by more fluoride ions than is the case for Ar. Furthermore, the oxide ion had a more covalent state in case of the glass prepared in Ar than in CO: the cerium ion in the glass prepared in CO might be under a cationic condition, whereas that in Ar might be under anionic condition.

Therefore, the valency of the cerium ion with the less positive charge (close to 3+) in the glass prepared in CO might increase. The valency of the cerium ion with more positive charge (close to 4+) in the glass prepared in Ar might decrease. For this reason, the two peak patterns of the glasses in Fig. 8 are similar.

Fig. 9 shows that the Ce4d spectra of both glasses were also very similar. The peak near 105 eV is the peak corresponding to Si2p. The peaks at 109, 123, and 126 eV that appeared in the spectrum of CeO_2 were not observed in the spectra of the glasses (Fig. 9). Furthermore, the peak pattern of the glasses in Fig. 9 differed completely from that of CeF_3. The peak pattern for Ce4d electron in the glasses must be distinctive to the glass, as are the Ce3d spectra. Although it was small, the peak at 122 eV was detected in the glasses. This difference might arise from the difference of the valency of the cerium ion in the glasses.

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 490 nm (peak-3). The energy difference between peak-1 and peak-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 oxygen and fluorine in the glasses prepared in this study were more covalent and ionic, respectively, than those in simple oxide and fluoride compounds. The peak profiles for Ce3d and Ce4d electrons in the glasses prepared in CO and Ar were mutually similar. The peak patterns for Ce3d and Ce4d electrons in the glasses must be distinctive to the glass. The valency of the cerium ion in the glass prepared in CO might be less than that in Ar.

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. It was then placed onto molecular sieves and cooled with liquid nitrogen to be quenched. 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 black 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 Ltd.).

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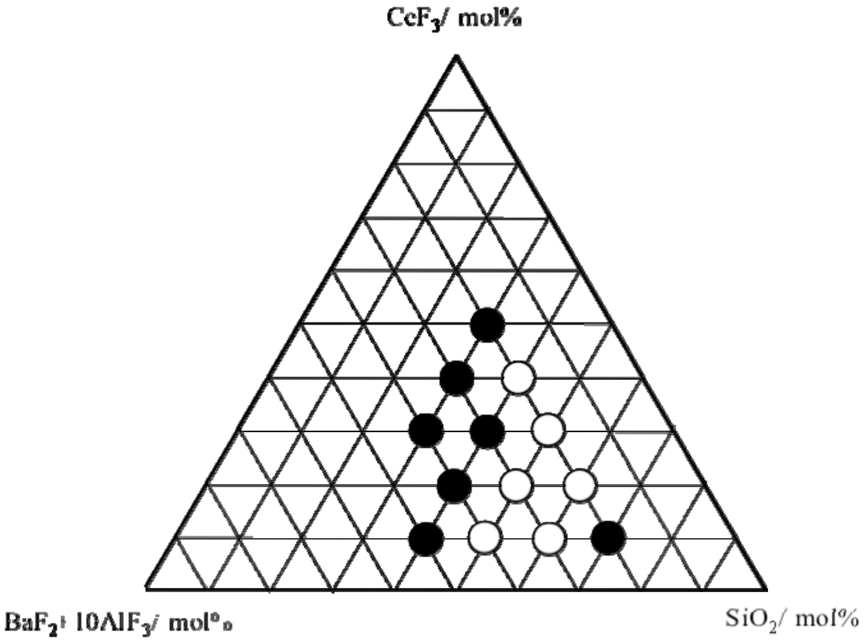

Fig. 1 Phase diagram of CeF_3-BaF_2-$10AlF_3$-SiO_2 system by nominal composition. Open and closed circles correspond to glass and not glass products, respectively.

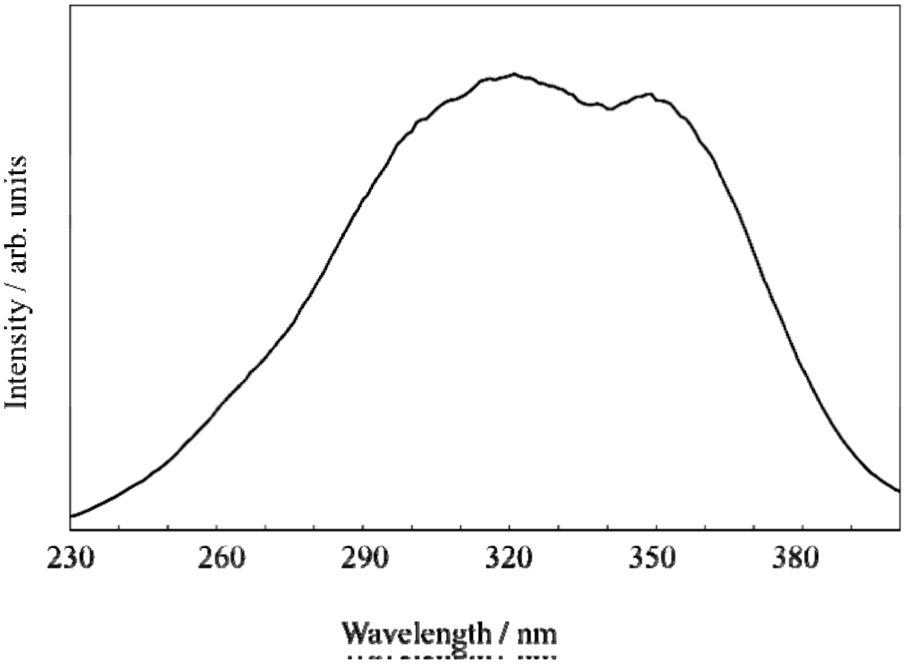

Fig. 2 Excitation spectrum of $10CeF_3$-$20BaF_2$-$10AlF_3$-$60SiO_2$ glass prepared in CO. The excitation spectrum under the emission wavelength at 435 nm.

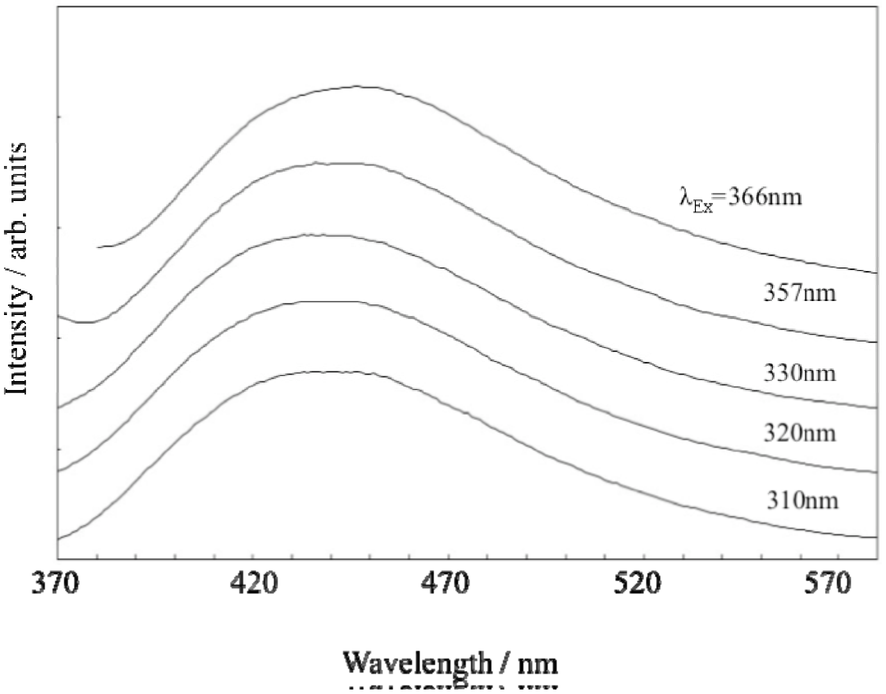

Fig. 3 Emission spectra of $10CeF_3$-$20BaF_2$-$10AlF_3$-$60SiO_2$ glass prepared in CO for several excitation wavelengths.

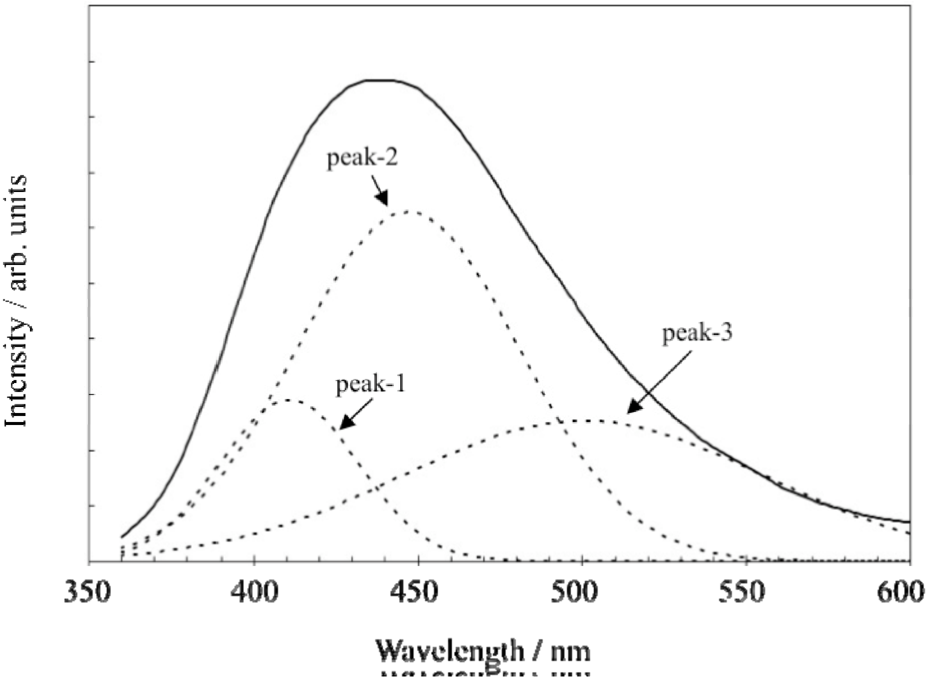

Fig. 4 Decomposition of the emission spectrum of $10CeF_3$-$20BaF_2$-$10AlF_3$-$60SiO_2$ glass prepared in CO under the excitation wavelength at 320nm. The solid line shows observed spectrum. The dashed lines show calculated spectra.

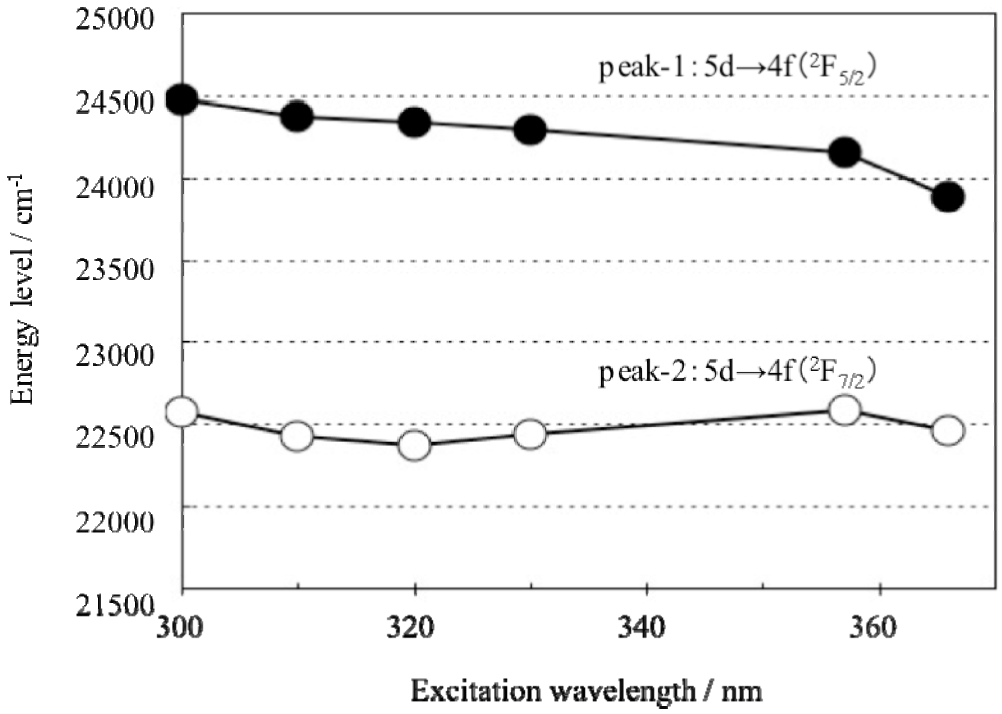

Fig. 5 Energy differences of peak-1 and peak-2 for several excitation wavelengths of $10CeF_3$-$20BaF_2$-$10AlF_3$-$60SiO_2$ glass prepared in CO.

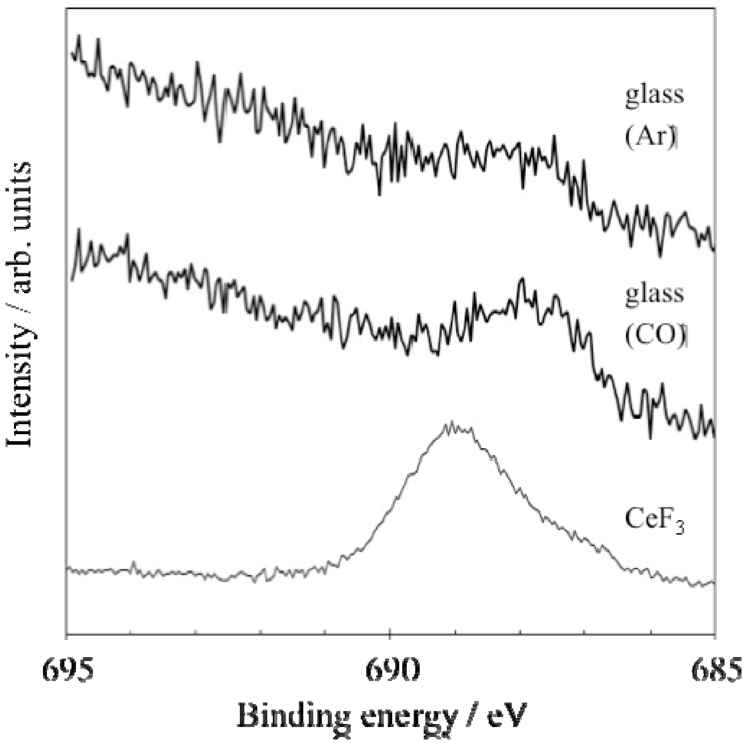

Fig. 6 F1s spectra of CeF_3 and $10CeF_3$-$20BaF_2$-$10AlF_3$-$60SiO_2$ glasses prepared in CO and Ar atmospheres.

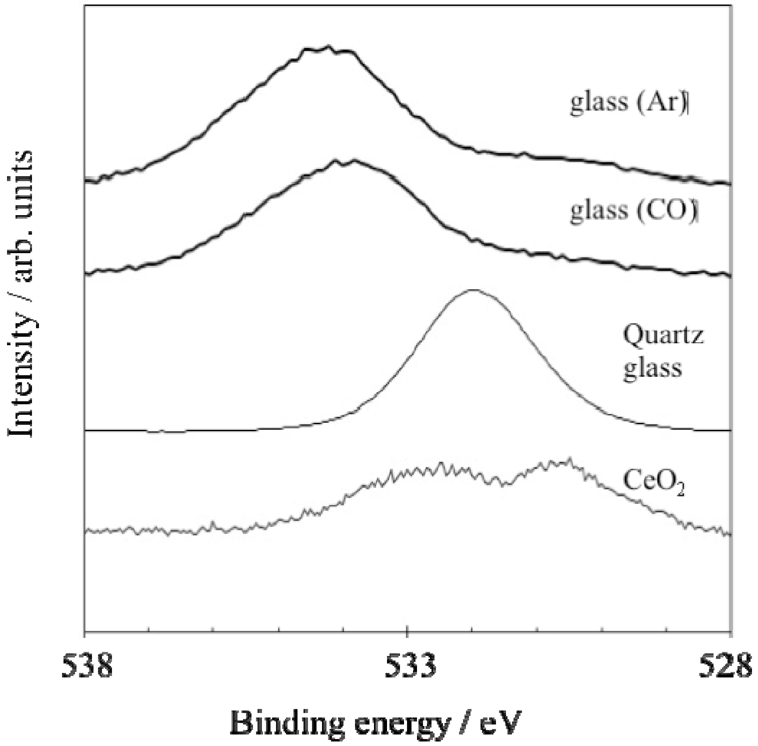

Fig. 7 O1s spectra of CeO_2, Quartz glass and $10CeF_3$-$20BaF_2$-$10AlF_3$-$60SiO_2$ glasses prepared in CO and Ar atmospheres.

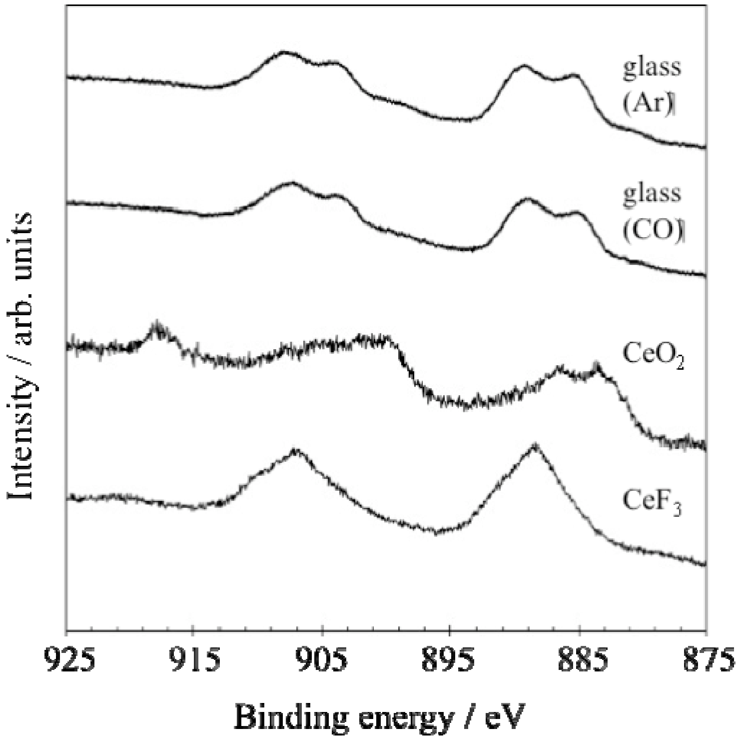

Fig. 8 Ce3d spectra of CeF_3, CeO_2 and $10CeF_3$-$20BaF_2$-$10AlF_3$-$60SiO_2$ glasses prepared in Ar and CO atmospheres.

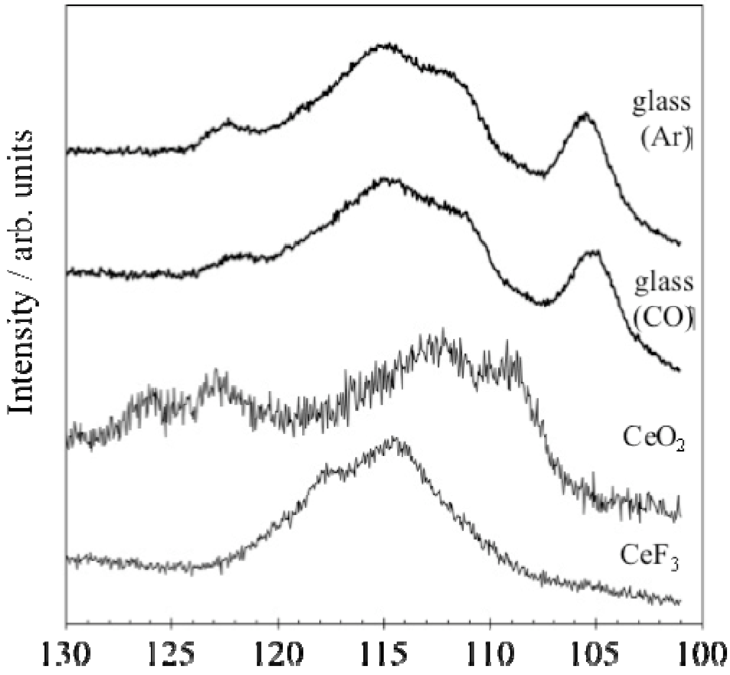

Fig. 9 Ce4d spectra of CeF_3, CeO_2 and $10CeF_3$-$20BaF_2$-$10AlF_3$-$60SiO_2$ glasses prepared in Ar and CO atmospheres.

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

	Peak-1			Peak-1			Peak-1		
λ_{Ex}	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	2539	411.61±0.78	48.12	60.24	445.71±3.98	77.01	27.65	495.07±23.74	121.49
357	1678	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