OPTICAL PROPERTIES OF Bi_2O_3-La_2O_3-Al_2O_3-B_2O_3 GLASSES

S. Sumimiya, T. Nanba, and Y. Miura
Department of Environmental Chemistry and Materials, Faculty of Environmental Science and Technology, Okayama University
3-1-1, Tsushima-Naka
Okayama-shi 700-8530, Japan

S. Sakida
Environmental Management and Safety Section, Health and Environment Center, Okayama University
3-1-1, Tsushima-Naka
Okayama-shi 700-8530, Japan

ABSTRACT

We investigated infrared luminescent phenomena in bismuth lanthanum borate glasses. In bismuth lanthanum borate glasses, the absorption peak was observed at 460 nm. The absorption peak was observed only when the glass was melted in Al_2O_3 crucible, whereas no peak was seen in the case of Pt crucible and the case of Al_2O_3 doped sample melted in Pt crucible. The infrared emission peak was observed at 1300 nm excited at 800nm. Life time at 1300 nm was 56.7 µs. We suggested that the absorption and infrared emission have been associated with pentavalent Bi ions in the glasses. It was estimated by La 3d XPS spectra and ESR spectra.

INTRODUCTION

Broad infrared luminescent materials can be used as a broadband amplifier and a high-power tunable laser, and hence the exploration of novel glass systems exhibiting a broad bismuth luminescence is extensively continued. Fujimoto and Nakatsuka[1] found an infrared luminescence of bismuth in $0.3Bi_2O_3$-$2.2Al_2O_3$-$97.5SiO_2$ glass, where the luminescence was observed at 1300 nm and the full width at half maximum (FWHM) was over 200 nm. They suggested that the infrared emission was associated with pentavalent Bi ions in the glass. Peng and Qiu[2] also reported the infrared luminescence in $1Bi_2O_3$-$3Al_2O_3$-$96GeO_2$ glass, and they concluded that the infrared emission was associated with monovalent Bi ions in the glass. Thus, the infrared luminescence was assigned to the different valence states of Bi ions.

In this study, the valence and electronic states of Bi ions in Bi_2O_3-La_2O_3-Al_2O_3-B_2O_3 glasses were investigated, from which the origin of the broad infrared luminescence was clarified.

EXPERIMENTAL

The compositions of glasses prepared in this study and melting temperatures are shown in Table 1. Reagent grade powders of La_2O_3, B_2O_3, Bi_2O_3, and Al_2O_3 were weighed, and the 10 g batches were melted in Pt or Al_2O_3 crucibles for 40 minutes. The melts were poured onto a brass plate and quickly pressed by a stainless steel plate. The glasses were polished before optical measurements. As described below, infrared luminescence was observed only in the glasses melted in Al_2O_3 crucible. Then, in order to examine the influence of Al_2O_3, 6mol% Al_2O_3 doped glasses were also prepared by using a Pt crucible, where Al_2O_3 content was determined from energy dispersive X-ray (EDX) analyses.

Optical absorption spectra (190 ~ 2500 nm) were measured on a spectrophotometer

(JASCO, V-570) at room temperature. Diffuse reflection spectra were also measured by the same spectrophotometer equipped with an integrating sphere using the powder samples. Infrared luminescence spectra were measured at room temperature by using an InP/InGaAs photo multiplier: excitation wavelength = 800 nm, and detection wavelength = 1100 ~ 1500 nm. X-ray photoelectron spectroscopic (XPS) measurements were performed by an S-Probe ESCA SSX-100S (Fisons Instruments). Electron spin resonance (ESR) spectra were collected at room temperature on Bruker ESP 300E working at 9.4 GHz (X-band) in the magnetic field of 0 ~ 5000 G.

Table 1. The compositions of glasses and melting conditions

Sample name	Composition [mol%]				Melting temperature [°C]	Crucible
	La_2O_3	B_2O_3	Bi_2O_3	Al_2O_3		
Host	22	78			1250	Al_2O_3
1Bi_Al_1250	22	78	1		1250	Al_2O_3
2Bi_Al_1250	22	78	2		1250	Al_2O_3
3Bi_Al_1250	22	78	3		1250	Al_2O_3
4Bi_Al_1250	22	78	4		1250	Al_2O_3
4Bi_Al_1450	22	78	4		1450	Al_2O_3
4Bi_Al_1650	22	78	4		1650	Al_2O_3
4Bi_Pt_1250(Al)	22	78	4	6	1250	Pt
5Bi_Al_1250	22	78	5		1250	Al_2O_3
20Bi_Al_1150	15	65	20		1150	Al_2O_3
20Bi_Al_1250	15	65	20		1250	Al_2O_3
20Bi_Al_1350	15	65	20		1350	Al_2O_3
20Bi_Pt_1150	15	65	20		1150	Pt
20Bi_Pt_1150(Al)	15	65	20	6	1150	Pt
20Bi10La_Al_1150	10	65	20		1150	Al_2O_3
20Bi5La_Al_1150	5	65	20		1150	Al_2O_3

RESULT

Optical absorption

Typical optical absorption spectra of Bi_2O_3-La_2O_3-B_2O_3 glasses are shown in Fig. 1. The optical absorption edge of the "Host" glass is located at about 3.5 eV, and the absorption edge shifts to lower energy side with increasing Bi_2O_3 content. In the glasses with Bi_2O_3, a peak was clearly observed at 2.7eV (460 nm), and the baseline became higher with increasing in Bi_2O_3 content. Hence, the diffuse reflection measurements were also done with the powdered specimens to ascertain the presence of the peak. The 2.7 eV peak was observed only in the glasses melted in Al_2O_3 crucibles. As shown in Fig. 1, the 2.7 eV peak increases in intensity with increasing Bi_2O_3 content (Fig. 1a) and melting temperature (Fig. 1b). In the glasses melted in a Pt crucible, the peak did not appear even when Al_2O_3 was added to the raw materials.

According to Nanba et al.,[3] the optical absorption edge is observed at around 2.0 eV in the bismuthate crystals containing Bi^{5+}. In the present glasses containing the different amount of La_2O_3, "20Bi_Al_1150", "20Bi10La_Al_1150", and "20Bi5La_Al_1150", the 2.7 eV peak increased in intensity with decreasing La_2O_3 content (not shown in Fig. 1), indicating that the peak was unrelated to La ions. It is tentatively concluded that the 2.7 eV peak is attributed to the optical absorption of Bi^{5+} ions.

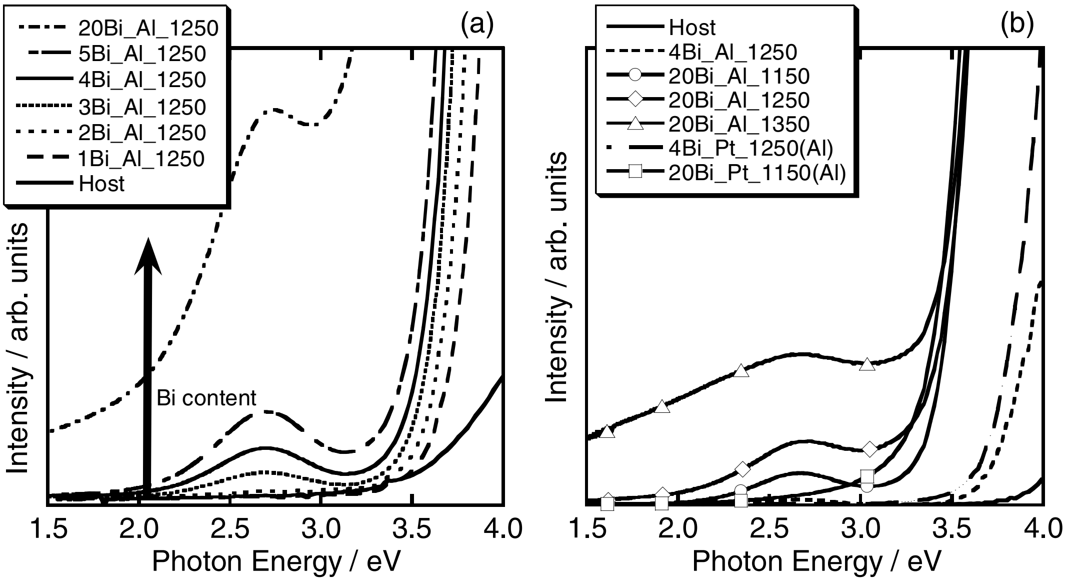

Fig. 1. Optical absorption spectra for Bi_2O_3-La_2O_3-B_2O_3 glasses.
(a) bulk glass, (b) powdered glass (diffuse reflection measurement)

Infrared luminescence

A typical infrared luminescent spectrum is shown in Fig. 2. A broad peak is observed at 1300 nm, and sharp peaks also appear at 1170 and 1250 nm. These two peaks were also confirmed in the Bi-free “Host” glass. Therefore, these two peaks are unrelated to the Bi-luminescence. The origin of the peaks is still unclear. The 1300 nm emission is seen only for the glasses melted in Al_2O_3 crucible.

A typical fluorescent decay curve is shown in Fig. 3. The decay curve was fitted by an exponential function to obtain the life time of emission. The life time of the glass shown in Fig. 3 is 56.7 μs. As compared with the references,[1, 2] the peak position is almost the same, but the life time is much shorter. The life time increases with increasing the luminescence intensity.

In the glasses containing 4mol% Bi_2O_3, the luminescence intensity increased as the melting temperature increased. However, in the glasses containing 20mol% Bi_2O_3, the luminescence intensity decreased with raising the melting temperature. If the 2.7 eV peak observed in the absorption spectra is related to the 1300 nm infrared emission, the decrease in luminescence intensity is probably due to the concentration quenching. Furthermore, if the 2.7 eV absorption peak is due to Bi^{5+} ions, also the 1300 nm emission may be caused by Bi^{5+} ions.

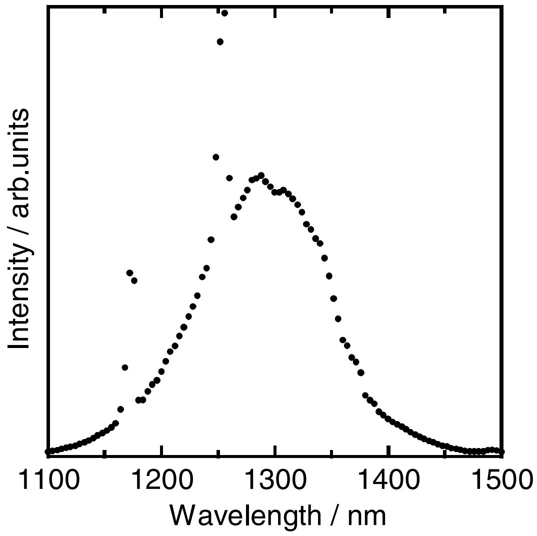

Fig. 2. A typical infrared luminescent spectrum.
Sample: 4Bi_Al_1250, excitation: 800 nm.

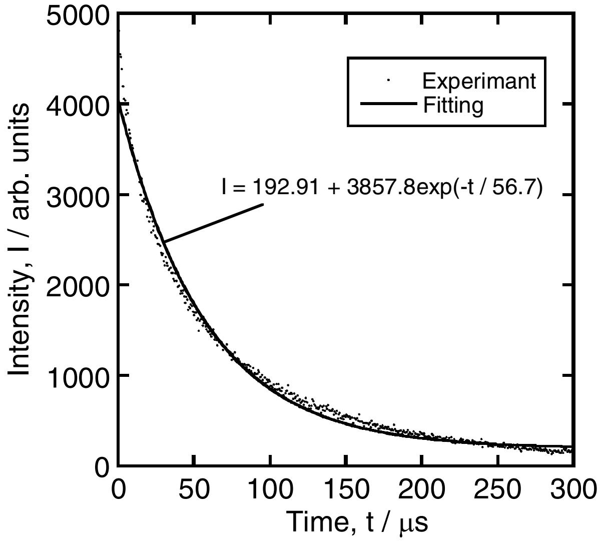

Fig. 3. A typical fluorescent decay curve.
Sample: 4Bi_Al_1250, excitation: 800 nm, emission: 1300nm.

XPS measurement

Fig. 4 shows the La 3d XPS spectra, where the La 3d signal splits into two components assigned to La $3d_{3/2}$ and $3d_{5/2}$. Furthermore, each component split into two more fragments, indicating that La ions are in mixed-valence state. It is known that La takes the oxidation number of 2 besides 3. Therefore, the low energy fragments in Fig. 4 are attributed to La^{2+}. The relative amount of La^{2+} is estimated as about 50%, which is independent of the melting temperature.

As for Bi, the most common oxidation number is 3, and Bi also takes the pentavalent state. In the infrared luminescence, the presence of Bi ions in monovalent state is also proposed.[2] Bi 4f XPS signals in the present glasses changed shape during the measurements. Hence, the valence state of bismuth ions could not be evaluated from XPS. As for La 3d and O 1s XPS signals, such the modifications in spectral shape were not observed.

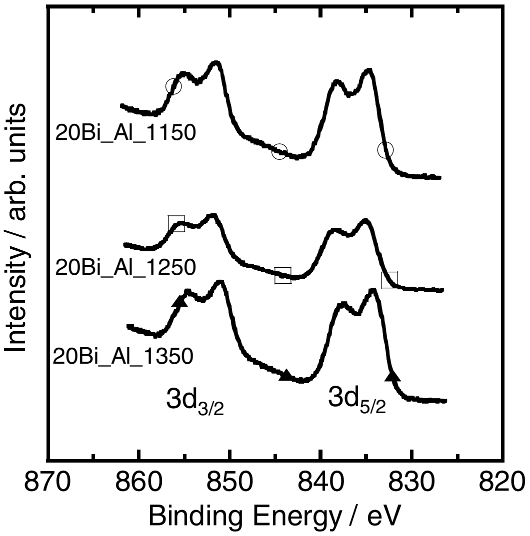

Fig. 4. La 3d XPS spectra for Bi_2O_3-La_2O_3-B_2O_3 glasses.

ESR measurement

ESR spectra of Bi_2O_3-La_2O_3-B_2O_3 glasses are shown in Fig. 5. Two signals are observed at $g = 4.2$ and 2.0. Similar ESR signals have been observed in Bi_2O_3-Li_2O glasses,[4] in which the signals at $g = 4.3$ and 2.1 were assigned to the transitions of $\Delta m_s = \pm 2$ and ± 1, respectively, in a triplet state created by the pairs of positive holes on the neighboring oxide ions (m_s: eigenvalue of the spin of magnetic field direction). The ESR signals confirmed in the present glasses are also attributed to the triplet center formed by the pairs of positive holes on oxide ions. Due to the so-called "powder pattern", the $g = 2.0$ signal is probably indistinct. It is also supposed that the zero-field splitting parameter D is not negligible in the present glasses, and the broad distribution in the distance between the positive holes leads to a wide distribution in D, resulting in the indistinct $g = 2.0$ signal.

The presence of Bi^+ is also proposed.[2] Bi^+ ion has unpaired electrons as $6p^2$, which is a candidate of the ESR triplet center. In the case of Bi^+ ion, however, the unpaired electrons are present on the same ion so that D must be quite large. At that case, the $g = 2.0$ signal will be broadened, and no signal is observed at $g = 2.0$. It is finally concluded that the possibility of Bi^+ is undeniable but the positive hole pairs are surely present in the glasses.

La^{2+} ions have an electronic configuration of $[Xe]5d^1 6s^0$, and hence they are ESR active. However, it is suggested from XPS that the concentration of La^{2+} ions in the present glasses is quite large, and it is therefore expected that the La^{2+} ESR signal is quenched and no signal is observed. Thus, the presence of La^{2+} ions in the present glasses is not confirmed by ESR.

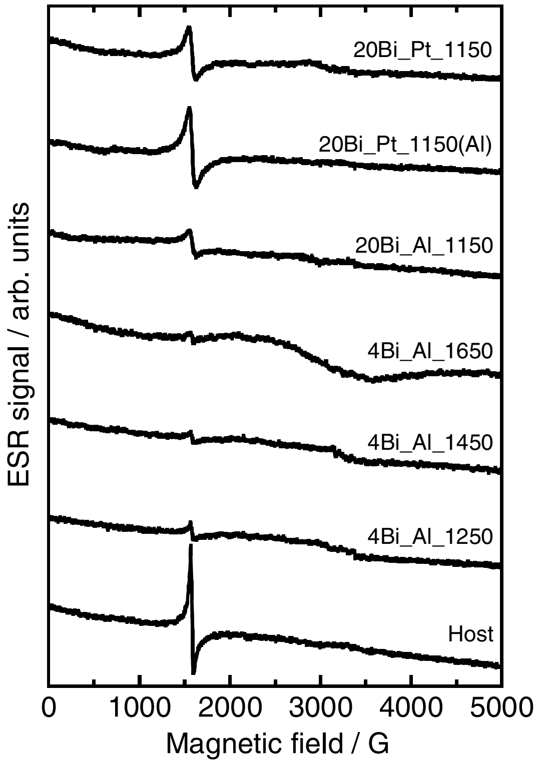

Fig. 5. ESR spectra for Bi_2O_3-La_2O_3-B_2O_3 glasses.

DISCUSSION

From the experimental results, the presence of following species were suggested, Bi^{5+} ions, La^{2+} ions, and positive holes on oxide ions. It was also suggested from XPS measurements that the valence states of La and oxide ions are stable but that of Bi ions is unstable in vacuum. It is therefore assumed that oxide ions donate electrons to La^{3+} ions, forming positive holes on oxide ions and La^{2+} ions, and the electron transfers take place mostly between La and oxide ions. On the other hand, the infrared luminescence is supposed to be associated with Bi^{5+} ions. There seems to be no causal association between the formations of La^{2+} and Bi^{5+} ions. It was observed that the $g = 4.2$ ESR signal decreased as the infrared emission increased, suggesting that the positive holes on oxide ions and Bi^{5+} ions had some correlations.

According to the molecular orbital calculations,[5] the positive holes on oxide ions and Bi^{5+} ions were related as follow; octahedral BiO_6 units are unstable because of large anti-bonding overlaps between Bi 6s and O 2p orbitals at around HOMO levels. If electrons are removed from the anti-bonding orbitals, the BiO_6 units become stable. There are two ways to remove electrons from the anti-bonding orbitals, that is, the removal of electrons from Bi 6s orbital to form Bi^{5+} ions and the removal of electrons from O 2p orbital to form positive holes on oxide ions. In Li_2O-B_2O_3 glasses, however, Bi^{5+} ions were not confirmed.[3] It is consequently supposed that the larger amount of positive holes on oxide ions associated with La^{2+} ions make Bi^{5+} ions stable.

The infrared luminescence was observed only when the glasses were melted in Al_2O_3 crucible, and the luminescence intensity increased with increasing the melting temperature, indicating that Al_2O_3 crucible was required for the formation of Bi^{5+} ion. In the glasses melted in Pt crucible, reduction of Bi ions into metallic state was sometimes observed, suggesting that Bi ions were not oxidized in Pt crucible. It is finally concluded that the infrared luminescence in the present glasses are caused by Bi^{5+} ions.

CONCLUSION

Infrared luminescence was observed in Bi_2O_3-La_2O_3-Al_2O_3-B_2O_3 glasses. This peak was broad and its wavelength was 1300nm. Appearance of the luminescence was due to Bi^{5+} ions. The applications to a broadband infrared amplifier and a high-power tunable laser will be expected if the study based on this conclusion will be continued. We need the further exploration of novel glass systems exhibiting a broad bismuth luminescence.

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