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Letter

Effects of halides on luminescence behaviors of Ce^{3+} ions in chalcohalide glasses

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ABSTRACT

We report photoluminescence of Ce^{3+} ions in GeS_2–Ga_2S_3–CsH (H = Cl, Br, I) chalcohalide glasses. Halides exert a major effect on luminescence behaviors of Ce^{3+} center in chalcohalide glasses with respect to both intensity and wavelength. In particular, the Ce^{3+} doped chalcohalide glass containing CsBr exhibits an intense broad emission in the green-yellow region which is much enhanced and experiences an obvious blue shift with the increase of the CsBr content. The origin of these unique luminescence behaviors is discussed in detail according to the formation of $[GaS_{3/2}Br]^-$ structural units and the optical basicity theory. The former reduces the phonon energy of glass matrix, thus increasing the luminescence efficiency, while the latter explains well the sensitivity of Ce^{3+} emission to the environment where Ce^{3+} ions locate.

1. Introduction

Recently there is a remarkable growth of research in rare-earth (RE) doped luminescent materials because of their unique optical properties for potential applications such as fluorescent lamps, solid-state lasers, flat panel display and so on [1–9]. Luminescence of these RE ions result from the electronic transitions occurring within the partially filled 4f energy shell of the lanthanide series [1] where the Ce^{3+} ion with a $4f^1$ configuration shows a specific 4f–5d transition. As 5d orbital is in the condition of non-shield, the electronic transition between this energy gap of Ce^{3+} ions is strongly dependent on ligand field strength, and hence, luminescence may occur over a very broad spectral range [8]. Besides, Ce^{3+} ion has a larger Stokes shift than other RE ions due to the extended radial wave functions of the 5d state [9]. For instance, high crystal field splitting or strongly covalent environments can decrease the energy of the down-converted photons, thus shifting the Ce^{3+} ion emission to the longer wavelength [10]. In line with it, when Ce^{3+} is incorporated in an oxide host lattice, the Ce^{3+} emission occurs in the wide wavelength region from UV to blue-green, depending on the covalent degree of the host [8,11–13]. Consequently, a systematic dependence of the Ce^{3+} emission wavelength on the enhancement of the covalent environments of Ce^{3+} ions is expected from oxide to the non-oxide systems. This prediction of the Ce^{3+} emission wavelength was recently exploited for the first time in the Ge–Ga–S–CsCl chalcohalide glasses and results demonstrated the red shift of the Ce^{3+} emission in comparison with the oxide or even oxynitride systems [9]. In the present work, we have further studied the effects of different halides on the Ce^{3+} luminescence behaviors in the Ge–Ga–S chalcogenide glasses by means of absorption and photoluminescence spectroscopy. In particular, CsBr gives rise to a fairly large decrease in multiphonon relaxation rates of the system [14–18] and the stronger covalent environments to cerium ions. Combination of these two factors favors the enhanced Ce^{3+} emission at the longer wavelength.

2. Experimental details

Ten bulk glasses were synthesized by conventional melt-quenching method employing the high-purity elements (Ge, Ga and S, 5N) or compounds (CsI, CsBr and CsCl, 3N) as raw materials. All raw materials were mixed according to the nominal compositions as listed in Table 1 which have been designed to satisfy the requirements of forming the stable and visible-transparent glasses. To establish the glassy domain, the mixtures (about 4 g) in the sealed silica ampoule under vacuum was heated to 980 °C in a rocking furnace for 12 h and quenched vertically in water. The obtained glass samples were annealed at the temperature near T_g for 2 h in order to remove inner stress. Samples with size of $Ø10 \times 2\,mm^3$ were well polished to achieve good optical quality. The absorption spectrum of the sample was performed by a Jasco V-570 spectrophotometer (JASCO International Co. Ltd., Tokyo, Japan.). The visible emission and excitation spectra were recorded by a Fluorolog-3-P UV–vis–NIR fluorescence spectrophotometer (Jobin Yvon, French). All optical measurements were carried out at room temperature.

3. Results and discussion

Figs. 1 and 2 present normalized visible absorption spectra of glass samples of different compositions. The absorption cut-off edge (λ_{vis}) of the glass matrix G1 is located at 415 nm while an obvious red shift of λ_{vis} is observed in the samples G3 (CsBr) and

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Table 1
Compositions (mol%) and Stokes shift Δλ (nm) of glass samples.

Sample No.	GeS_2	Ga_2S_3	CsCl	CsBr	CsI	Ce	Δλ
G1	70	15	15				
G2	70	15	15			0.08	75
G3	70	15		15			
G4	70	15		15		0.08	84
G5	70	15			15		
G6	70	15			15	0.08	90
G7	60	20		20		0.08	75
G8	55	27.5		17.5		0.08	76
G9	52.5	26.25		21.25		0.08	71
G10	50	25		25		0.08	67

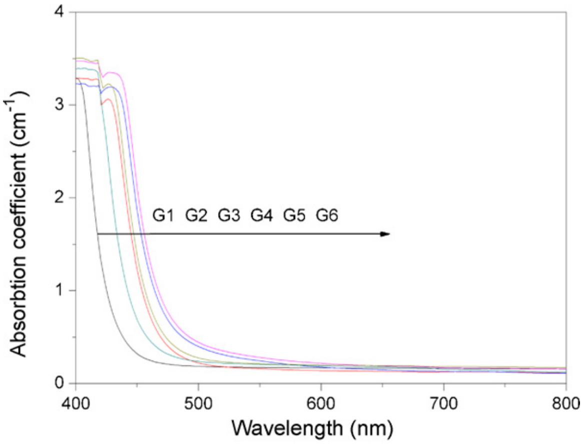

Fig. 1. Absorption spectra of samples G1–G6.

G5 (CsI) (Fig. 1). This is due to a decrease in electronegativity of those halides resulting in the narrower bandgap of glasses. On the other hand, the red shift occurs with the doping of Ce^{3+} ions in the GeS_2–Ga_2S_3–CsBr glasses (Fig. 1) and goes on with the substitution of CsBr by GeS_2 or Ga_2S_3 (Fig. 2). This is because that the Ce^{3+} 4f–5d transition is sensitive to the covalent surroundings [10]. With the help of the concept of optical basicity (OB) that represents the electron donor power (EDP) of an oxide in oxide glasses, we know that the OB of the present chalcohalide glasses increases with the decrease of the CsBr and increases of GeS_2 or Ga_2S_3 because of S having the higher EDP due to the lower electronegativity than Br. Higher OB of the glass matrix gives rise to an overall increase of negative charge to Ce^{3+} ions and allows an outermost electron to be promoted more readily into the 5d level, thus leading to the longer λ_{vis}.

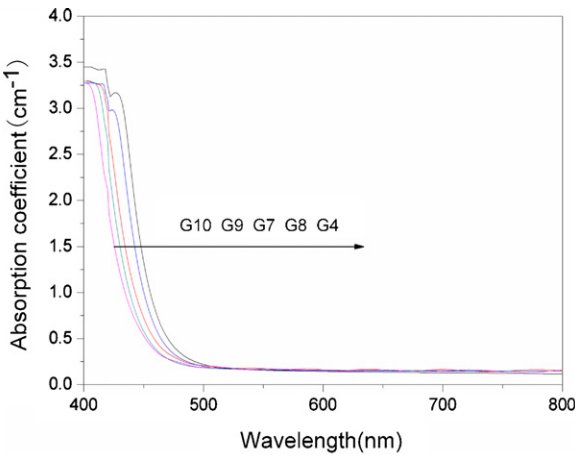

Fig. 2. Absorption spectra of samples G4 and G7–G10.

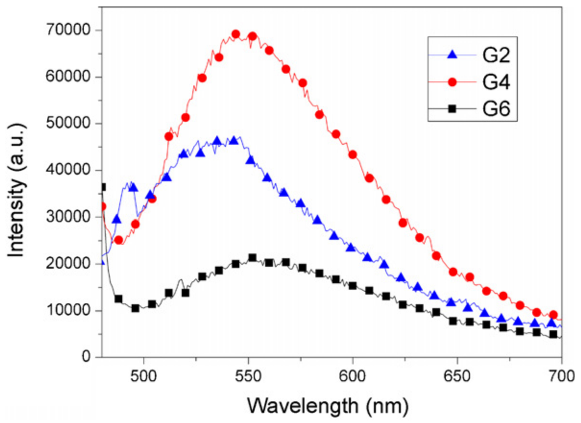

Fig. 3. Emission spectra of samples (G2, G4, G6) with different halides and their excitation wavelengths are 460, 465 and 470 nm, respectively.

Figs. 3 and 4 show the emission and excitation spectra of Ce^{3+} doped samples G2, G4, G6 with different halides, respectively. The emission spectra of all samples are characterized by a broad emission band (λ_{em}) covering a fairly large wavelength region from blue to red. The emission is due to the d–f[$^4f_0{}^5d_1 \rightarrow {}^4f_1(^2F_J)$] transition of Ce^{3+} ion from 5d excited state to ^2F ground state being regarded as the parity allowed electric dipole (e–d) transition with large oscillator strength [9]. As mentioned above, 4f-5d electron transition of Ce^{3+} ions is sensitive to the environment. Therefore, with the increased covalent degree of the host in the order of G2, G4 and G6, an obvious red shift occurs to λ_{em}. Another important observation is that the sample containing CsBr (G4) presents the strongest luminescence intensity among all three samples. We suppose the possible reason being associated with the formation of $[GaS_{3/2}Br]^-$ structural units due to addition of CsBr in the Ge–Ga–S system glasses as demonstrated by extended X-ray absorption fine structure (EXAFS) [14,16]. As $[GaS_{3/2}Br]^-$ units has the lower phonon energy than $GeS_{4/2}$ tetrahedra and $GaS_{3/2}$ triangles, they tend to reduce the multiphonon relaxation (MPR) rates of the matrix, thus increasing the quantum efficiency of Ce^{3+} emission. Although CsI has the lower phonon energy than CsCl and CsBr, it has the poorest glass-forming ability in chalcohalide glasses among all three halides [19,20]. Comparison of XRD spectra (which are omitted here) between samples G4 and G6 demonstrates an existence of a small amount of crystals in G6. This may deteriorate the homogeneity of the glass, produces the scattering loss, and consequently,

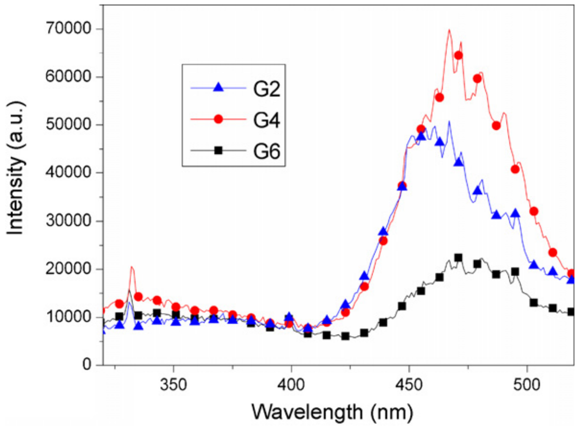

Fig. 4. Excitation spectra of samples (G2, G4, G6) with different halide and monitoring wavelengths of their excitation spectra are 535, 549 and 560 nm, respectively.

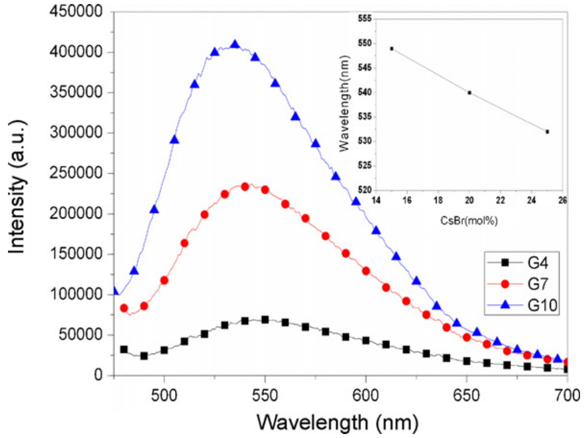

Fig. 5. Emission spectra of samples (G4, G7, G10) with different compositions (Ga_2S_3:CsBr = 1:1). Excitation wavelength of emission spectra is 465 nm. The inset shows the emission peak (*y*-axis) shifts with the variety content of CsBr (*x*-axis).

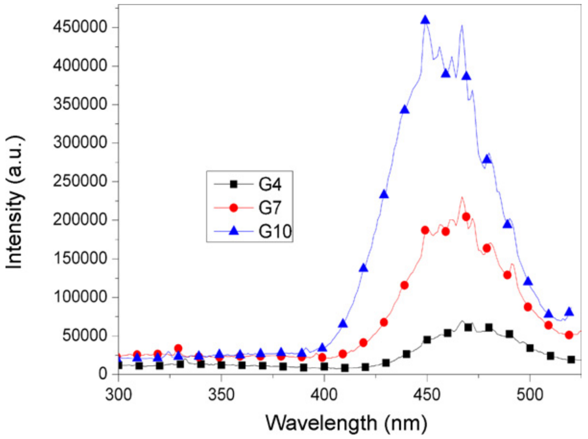

Fig. 6. Excitation spectra of samples (G4, G7, G10) and monitoring wavelengths of their excitation spectra are 549, 540 and 532 nm, respectively.

results in the decrease of the Ce^{3+} emission intensity. The excitation spectra show the similar phenomenon in both band position and intensity, as shown in Fig. 4.

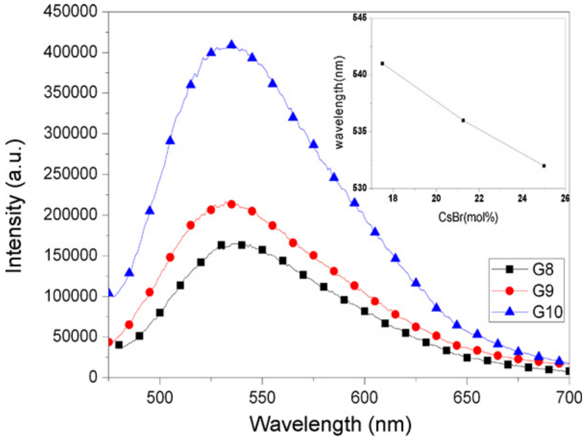

Fig. 7. Emission spectra of samples (G8, G9, G10) with different compositions (GeS_2:Ga_2S_3 = 2:1). Excitation wavelength of emission spectra is 465 nm. The inset shows the emission peak (*y*-axis) shifts with the variety content of CsBr (*x*-axis).

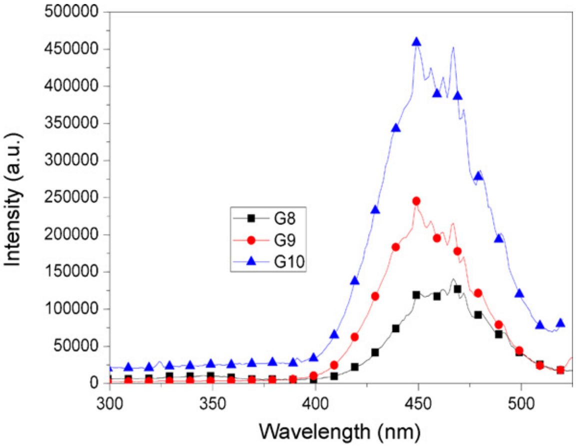

Fig. 8. Excitation spectra of samples (G8–G10) and monitoring wavelengths of their excitation spectra are 541, 536 and 532 nm, respectively.

Figs. 5–8 show the emission and excitation spectra of samples with the ratios of Ga_2S_3/CsBr and GeS_2/Ga_2S_3 fixed at 1:1 and 2:1, respectively. On the other hand, they have the content of CsBr varying from 15 to 25 mol% (as shown in Table 1) and the concentration of the Ce^{3+} ions fixed at 0.08 mol% [9]. In both cases, the increase of CsBr content results in a blue shift of λ_{em} in the range of 532–549 nm (insets), and at the same time, the much enhanced Ce^{3+} emission. The spectral shift can be explained similarly as above on the absorption spectra (Figs. 1 and 2) as well as on the emission spectra of samples with different halides (Fig. 3). Because the more substitution of sulfides by CsBr, the lower the OB of the glass matrix, and the lower the covalent environment to Ce^{3+} ions. Therefore, Ce^{3+} ions produce emission at the shorter wavelength. The enhancement of Ce^{3+} emission with the increased CsBr content is identical to the Ce^{3+} emission behavior as shown in Fig. 3. With the increased CsBr content, more $[GaS_{3/2}Br]^-$ units are formed, which reduces an overall phonon energy of the glass matrix, leading to the enhanced Ce^{3+} emission. Another possible reason is related to the so-called Urbach-Edge-Absorption-Assistant (UEAA) excitation due to partially overlapped intrinsic optical transitions of the glass matrix with the 4f–5d shell transitions of Ce^{3+} ions [21]. As discussed above, a blue shift of the λ_{vis} resulting from the increased CsBr content leads to the increased overlapping area of the Urbach edge of the host glass with the 4f–5d transitions of Ce^{3+} ions. Therefore, the energy transfer process from the host to the Ce^{3+} ions is enhanced, resulting in the higher luminescence intensity.

The excitation spectra show a similar increase in intensity but little spectral shift. The latter indicates that Stokes shift $\Delta\lambda$ ($\lambda_{em} - \lambda_{ex}$) increases with the decreased CsBr content in the host. Another characteristic feature of the excitation spectra is the expected doublet bands arising from the transition between 5d and $^2F_{5/2}$ and $^2F_{7/2}$ levels due to spin orbit splitting of the $4f^1$ ground state of Ce^{3+} ions as reported in certain glasses and phosphors [22–24]. However, doublet bands disappear with the decrease of CsBr content, indicating that the decreased CsBr content increases the disorder degree of chalcogenide glasses. Therefore, inhomogeneous broadening effect on the optical transitions of activators becomes more notable, resulting in disappearance of doublet bands replaced by a broad one.

4. Conclusions

In summary, effects of halides (CsCl, CsBr, CsI) on luminescence behaviors of Ce^{3+} ions in the Ge–Ga–S system glasses are studied for the first time. The CsBr containing glass presents the strongest luminescence intensity of Ce^{3+} ions among all three halides. With the increase of CsBr content, the Ce^{3+} emission is much enhanced due to the formation of more $[GaS_{3/2}Br]^-$ structural units which reduces the phonon energy of glass matrix, thus decreasing the

MPR and increasing the quantum efficiency of Ce^{3+} emission. The spectral shift with CsBr content is also observed which is associated with the varied covalent degree of the host. Because the substitution of sulfides by CsBr decreases the OB of the glass matrix, the environment to Ce^{3+} ions becomes less covalent, therefore, the blue spectral shift occurs. The present work may find applications as luminescence materials in illumination devices.

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