Optical Properties of Au^- Centers in CsBr and CsI Single Crystals

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The temperature dependence of the absorption and luminescence spectra has been investigated for Au⁻ centers in CsBr and CsI single crystals with the CsCl structure. In addition to the A, B, C, and D absorption bands, the A' and B' luminescence bands caused by the intraionic transitions in the Au⁻ ion are observed at 12 K. The luminescence bands are characterized by a small Stokes shift and a narrow halfwidth, reflecting a weak electron-phonon interaction. Furthermore, the photoexcitation at the energies corresponding to the A, B, and C absorption bands induces luminescence bands in the visible energy region. The A', B', and visible luminescence bands change with temperature while complementing each other. The features of the Au⁻ centers in cesium halides and the nonradiative transitions between the relaxed excited states are discussed.

KEYWORDS: cesium halides, Au⁻ centers, luminescence properties, nonradiative transitions

1. Introduction

Alkali halide crystals doped with ions that have the $n\text{s}^2$ electronic configuration in their ground state exhibit several absorption bands below the fundamental absorption edge of host crystals.[1–4] These absorption bands are labeled A, B, C, and D in order of increasing photon energy. The A, B, and C absorption bands are attributed to intraionic transitions from the ground $^1\text{S}_0$ state to the excited $^3\text{P}_1$, $^3\text{P}_2$, and $^1\text{P}_1$ states in the $n\text{s}^2$-like ions, respectively. The $^1\text{S}_0 \rightarrow {}^1\text{P}_1$ transition is a dipole allowed transition. The $^1\text{S}_0 \rightarrow {}^3\text{P}_1$ and $^1\text{S}_0 \rightarrow {}^3\text{P}_2$ transitions are partially allowed by spin-orbit interaction and lattice vibrations, respectively. In the case of cationic $n\text{s}^2$ centers such as Tl⁺, In⁺, and Pb²⁺, the D bands are attributed to the exciton transitions perturbed by the $n\text{s}^2$-like ion and/or the charge transfer transitions from a halogen ion to the $n\text{s}^2$-like ion.[3–6] When the alkali halide crystals doped with the $n\text{s}^2$-like ions are irradiated by the photons with energies corresponding to the absorption bands, the luminescence bands caused by the radiative transitions from the relaxed excited states of $^3\text{P}_1$, $^3\text{P}_2$, and

$^1P_1$ appear with Stokes shifts.[2–4,7–10] These luminescence bands are called the A', B', and C' luminescence bands, respectively.

The optical properties of alkali halide crystals containing a small amount of ns^2 -like ions have been studied extensively since the pioneering work of Hilsch in 1927.[11] A number of theoretical and experimental studies have been performed on cationic ns^2 centers such as Tl^+, In^+, and Pb^{2+}.[1–4] As compared with the cationic ns^2 centers, the anionic ns^2 centers such as Au^-, Ag^-, and Cu^- are comparatively less studied,[12–21] especially the Au^- center in cesium halide crystals.

Among the ns^2 centers, only the Tl^+ centers in cesium halides exhibit unique absorption bands that cannot be explained by the intraionic transitions in the Tl^+ ion.[22–26] The appearance of the unique absorption bands has been considered to be due to the arrangement of the eight halogen ions around the Tl^+ ion in the CsCl crystal structure.[5,27] In our previous paper,[26] we suggested that the electronic states of the Tl^+ centers in the cesium halides are affected by the d states of the next-nearest-neighbor Cs^+ ions from a comparison with the absorption bands of the Tl^+ centers in ammonium halides with the CsCl crystal structure. The In^+ centers in cesium halides, which have the $5s^2$ outermost electron configuration, exhibit the A, B, and C absorption bands caused by the intraionic transitions.[28–30] This fact leads us to the idea that only the electronic states of the $6s^2$ centers in cesium halides are affected by the d states of the Cs^+ ions. The Au^- anion has the same $6s^2$ outermost electron configuration as the Tl^+ ion. Therefore, the comparisons of the optical properties between the Au^- and Tl^+ centers in cesium halides may provide new information on the cause of the unique absorption bands of the Tl^+ centers in cesium halides.

We reported the preliminary optical properties of the Au^- center in CsBr and CsI single crystals twenty years ago.[20] In the previous paper, the A, B, C, and D absorption bands due to the Au^- center and their relaxed luminescence bands were observed in the ultraviolet (UV) energy region at low temperatures. From the relative positions of the absorption bands and their relative intensity ratio, the Coulomb energy, the exchange energy, the spin-orbit interaction energy, and the King-Van Vleck parameter, which characterize the ns^2 centers, were obtained for the Au^- center in CsBr and CsI crystals. The effective energies of phonons interacting with the electronic states in the Au^- centers were also estimated from the temperature dependence of the halfwidths of the absorption and luminescence bands. However, the temperature dependence of the luminescence properties was not discussed in detail.

In this study, the absorption and luminescence properties of CsBr:Au^- and CsI:Au^- are investigated over a wide visible-to-UV energy region at a lower temperature than that in the

previous study. As a result, the energy positions, halfwidths, and effective phonon energies of the A, B, and C absorption bands are specifically confirmed. Furthermore, the measurements of the luminescence spectra in the visible energy region reveal the existence of new luminescence bands associated with the Au$^-$ center. The temperature dependence of the luminescence properties including new luminescence bands is discussed on the basis of the nonradiative transitions among the relaxed excited states.

2. Experimental Methods

Although gold has a large electron affinity of 2.54 eV, Au$^-$ ions are not naturally present in alkali halide crystals. Therefore, a special treatment is required to produce the Au$^-$ ions in the crystals.

Pure single crystals of CsI and CsBr were purchased from Union Material Incorporation (Japan). The incorporation of Au$^+$ ions into the pure single crystals was performed by a diffusion technique as described in previous papers.[12, 13] Conversion from the Au$^+$ cations to Au$^-$ anions was achieved by heating the crystals in potassium vapor or an electrolytic coloration technique. In order to remove F centers and create the isolated Au$^-$ centers, the samples cleaved to a size of $10 \times 10 \times$ about 0.5 mm^3 were wrapped in an aluminum foil and heated to about 500 °C for several minutes followed by fast cooling at RT through contact with a metal plate.

The samples were set on a cold stage of an optical cryostat, which was connected to a cryogenic refrigerator of the Cryo-Mini D type (Osaka Sanso Kogyo). Absorption measurements were performed by a combination of a grating monochromator (JASCO CT25CS) attached to a D$_2$ lamp as a light source and a photomultiplier (HAMAMATSU R-928). A 2 kW Xe lamp was used as an excitation light source for the measurement of the luminescence and excitation spectra. Luminescence from the sample was allowed to pass through another monochromator (Spex 270M) and was detected with a photomultiplier (HAMAMATSU R-955). The temperature dependence of the optical spectra was measured by heating the sample.

3. Experimental Results

3.1 Absorption spectra

We measured the absorption spectra of the samples with various Au$^-$ center concentrations. The Au$^-$ center concentrations were estimated to be 10^{16} - 10^{18} number/cm^3 from the absorption intensities of the A and C bands. Figure 1 shows the schematically drawn absorption spectra of CsBr:Au$^-$ and CsI:Au$^-$ crystals, which are drawn by composing the spectra
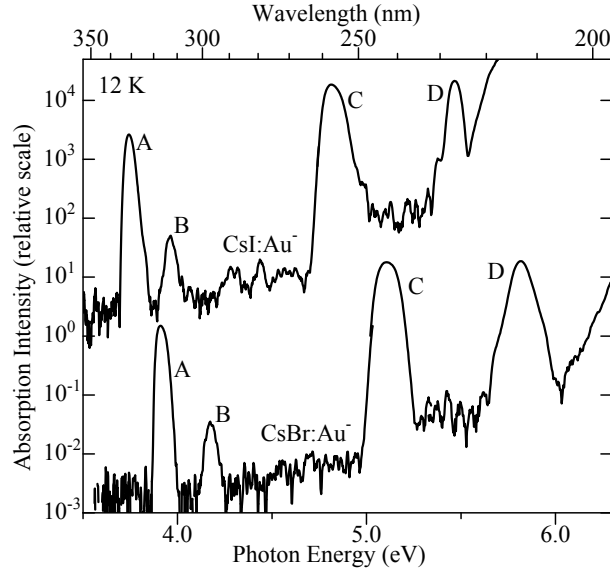
Fig. 1. Absorption spectra of CsBr:Au⁻ and CsI:Au⁻ single crystals. The spectra are drawn by composing the spectra of the samples with various Au⁻ center concentrations. The vertical axis of the figure is in the logarithmic scale. Measurements were performed at 12 K.

of the samples with various Au⁻ center concentrations. The A, B, and C absorption bands caused by the intraionic transitions in the Au⁻ center are observed in the energy region below the fundamental absorption edge of the bulk crystals. The peak energies and the halfwidths at low temperatures are summarized in Table I. The absorption bands peaking at 5.82 eV for CsBr:Au⁻ and at 5.46 eV for CsI:Au⁻ are assigned to the D band, which is attributed to the intraionic transition (5d) $\longrightarrow$ (6p) or (6s) $\longrightarrow$ (7p) in the Au⁻ ion.[13, 14, 17]

Figures 2(a) and 2(b) show the temperature dependence of the absorption spectra of CsBr:Au⁻ and CsI:Au⁻, respectively. The absorption bands exhibit a lower energy shift and broadening with increasing temperature. A distinct doublet structure due to the dynamic Jahn-Teller effect is observed for the A absorption bands at higher temperatures. The broadening of the absorption bands at each temperature is estimated in terms of the value of the second moment, which is calculated by moment analysis. As an example, the second moments of the A band in CsBr:Au⁻ and the C band in CsI:Au⁻ are plotted as a function of temperature in the insets of Figs. 2(a) and 2(b), respectively.

According to theoretical studies,[2, 31, 32] the temperature dependence of the second moment obeys the following equation:

$$M_2(T) = M_2(0) \coth \frac{h\nu}{2k_B T}, \tag{1}$$

where $M_2(0)$ is the second moment at 0 K and $h\nu$ is the effective phonon energy. The best
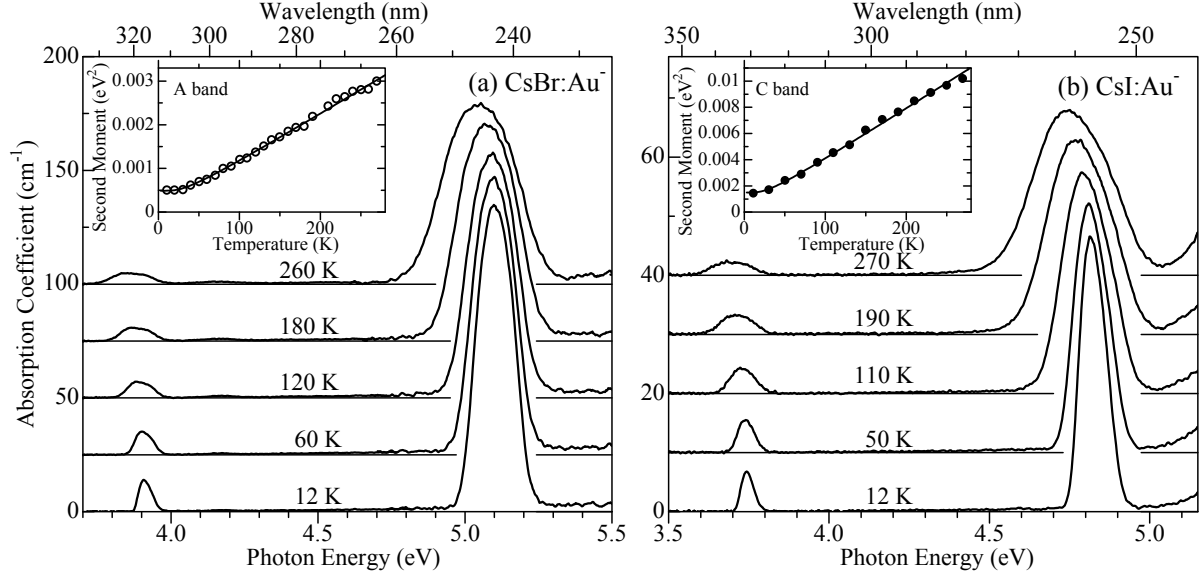
Fig. 2. Temperature dependence of the absorption spectra of (a) CsBr:Au⁻ and (b) CsI:Au⁻. Insets in (a) and (b) show the temperature dependence of the second moments of the A absorption band in CsBr:Au⁻ and the C absorption band in CsI:Au⁻, respectively. The solid lines in the insets show the best fitting results obtained using eq. (1).

Table I. Peak energies and halfwidths at low temperatures, and effective phonon energies $h\nu$ for the A, B, and C absorption bands in CsBr:Au⁻ and CsI:Au⁻. For comparison, the $h\nu$ values reported in the previous paper[20] are also listed.

		A	B	C
	peak energy (eV)	3.907	4.173	5.109
CsBr:Au⁻	halfwidth (eV)	0.052	0.048	0.133
	$h\nu$ (meV)	7.6 5.8[20]	7.4 7.4 to 10.3[20]	13.5 —
	peak energy (eV)	3.743	3.964	4.814
CsI:Au⁻	halfwidth (eV)	0.047	0.049	0.100
	$h\nu$ (meV)	10.3 7.8[20]	7.5 5.4 to 7.9[20]	6.6 —

fitting results are shown by the solid lines in the insets of Fig. 2. The effective phonon energy $h\nu$ values estimated from the temperature dependence of the second moment are also listed in Table I. The values for the A and B absorption bands agree with those reported in the previous paper.[20] The values for the C absorption bands are reported for the first time in the present work.
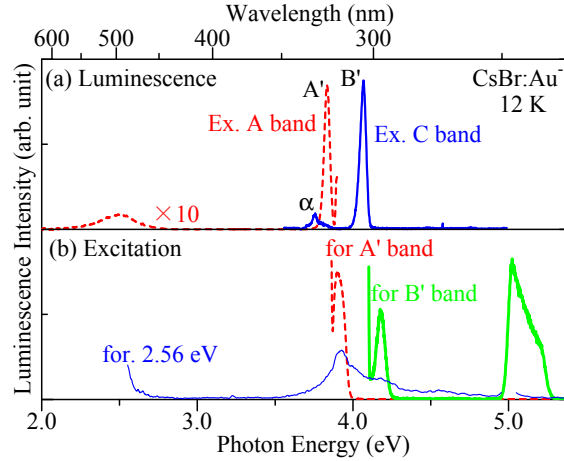
Fig. 3. (Color online) (a) Luminescence and (b) excitation spectra of CsBr:Au⁻ crystals at 12 K. The broken and solid lines in (a) correspond to the luminescence spectra under excitation at the A and C absorption bands, respectively. In (b), the thin solid, broken, and solid lines correspond to the excitation spectra for the 2.56 eV, A', and B' luminescence bands, respectively.

3.2 Luminescence and excitation spectra at low temperatures

The luminescence and excitation spectra of CsBr:Au⁻ crystals at 12 K are shown in Figs. 3(a) and 3(b), respectively. The excitation at the A and C absorption bands induces the sharp luminescence bands peaking at 3.837 and 4.062 eV, respectively. The 3.837 and 4.062 eV luminescence bands are assigned to the A' and B' luminescence bands, respectively.[20] The A' luminescence band has a sharp excitation band at the energy position of the A absorption band, while the B' luminescence band is efficiently excited at the energy positions of the B and C absorption bands.

In addition to the A' and B' luminescence bands, the weak luminescence bands peaking at 2.56 and 3.738 eV are observed under excitation at the A and C absorption bands, respectively. Since the 2.56 eV luminescence band has the excitation band around the energy position of the A absorption band, the 2.56 eV band would be associated with the $^3P_1$ state.

The small luminescence band peaking at 3.738 eV is located at the energy region below the A' luminescence band. In the Au⁻ centers in alkali halide crystals, the luminescence band called α is usually observed at the lower energy side of the A' luminescence band differently from other ns^2 centers in alkali halides.[14,17] The α luminescence bands have a decay time of about several 10 ms at low temperatures and are attributed to the transition from the relaxed excited state of $^3P_0$, which is located at the low-energy side of the relaxed $^3P_1$ state. Although the decay time of the 3.738 eV luminescence band in CsBr:Au⁻ is not measured, we assign that band to the α luminescence one.
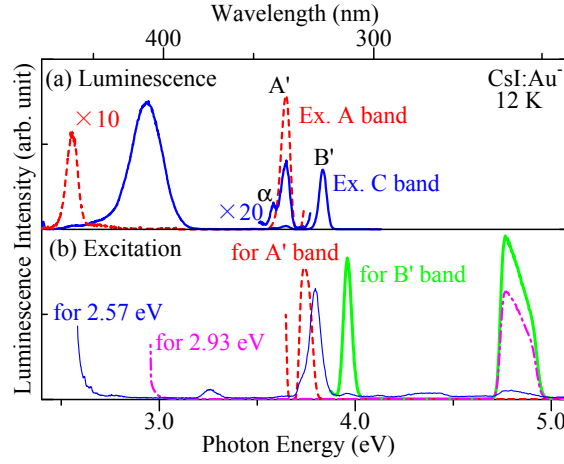
Fig. 4. (Color online) (a) luminescence and (b) excitation spectra of CsI:Au⁻ single crystals at 12 K. The broken and solid lines in (a) correspond to the luminescence spectra under excitation at the A and C absorption bands, respectively. In (b), the thin solid, dotted broken, broken, and solid lines correspond to the excitation spectra for the 2.57 eV, 2.93 eV, A', and B' luminescence bands, respectively.

Table II. Peak energies, halfwidths, and Stokes shifts of the A' and B' luminescence bands at low temperatures in CsBr:Au⁻ and CsI:Au⁻. The peak energies of the α band are also listed.

		α	A'	B'
	peak energy (eV)	3.738	3.837	4.062
CsBr:Au⁻	halfwidth (eV)		0.046	0.049
	Stokes shift (eV)		0.070	0.111
	peak energy (eV)	3.585	3.647	3.839
CsI:Au⁻	halfwidth (eV)		0.052	0.050
	Stokes shift (eV)		0.096	0.125

Figure 4 shows the luminescence and excitation spectra of CsI:Au⁻ at 12 K. There are five luminescence bands under excitation at the A and C absorption bands. Among these bands, the bands peaking at 3.647 and 3.839 eV are assigned to the A' and B' luminescence bands from the excitation spectra for both bands. The small luminescence band peaking at 3.585 eV is assigned to the α luminescence band. In addition to the luminescence bands described above, the luminescence bands comparable in intensity to the A' and B' luminescence bands are observed at 2.57 and 2.93 eV. These bands were not reported in our previous paper.[20] The excitation spectra for the 2.57 and 2.93 eV luminescence bands have pronounced excitation bands at the energy positions of the A and C absorption bands, respectively. Therefore, the
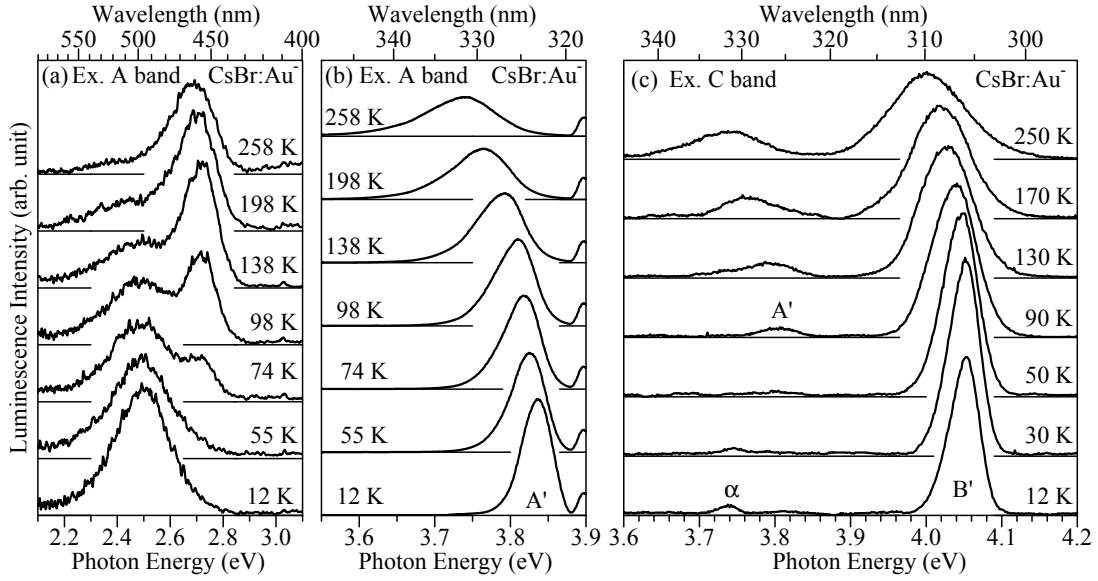
Fig. 5. Temperature dependence of the luminescence spectra of CsBr:Au⁻ in the visible energy region (a) and in the UV energy region (b) under excitation at the A absorption band. (c) corresponds to the temperature dependence of the luminescence spectra of CsBr:Au⁻ in the UV energy region under excitation at the C absorption band.

2.57 and 2.93 eV luminescence bands would be respectively related to the $^3P_1$ and $^1P_1$ states.

The peak energies, halfwidths, and Stokes shifts of the A' and B' luminescence bands in CsBr:Au⁻ and CsI:Au⁻ at low temperatures are summarized in Table II together with the peak energy of the α band. The C' luminescence band was not observed even under excitation at the C absorption band.

3.3 Temperature dependence of luminescence spectra of CsBr:Au⁻

Under excitation at the A absorption band, the temperature dependence of the luminescence spectra of CsBr:Au⁻ in the visible and UV energy region is shown in Figs. 5(a) and 5(b), respectively. As the temperature increases, the 2.56 eV luminescence intensity decreases and the luminescence band peaking at 2.70 eV appears. The 2.70 eV luminescence band grows in a complementary manner with a decrease in 2.56 eV luminescence intensity. As shown in Fig. 5(b), the A' luminescence band exhibits a redshift and becomes broad without any marked change in luminescence intensity.

Figure 5(c) shows the luminescence spectra at various temperatures under excitation at the C absorption band. The spectral changes at various temperatures are similar to that under excitation at the B absorption band. As the temperature increases from 12 K, the B' luminescence band at 4.32 eV exhibits a redshift and becomes broad. With increasing temperature,
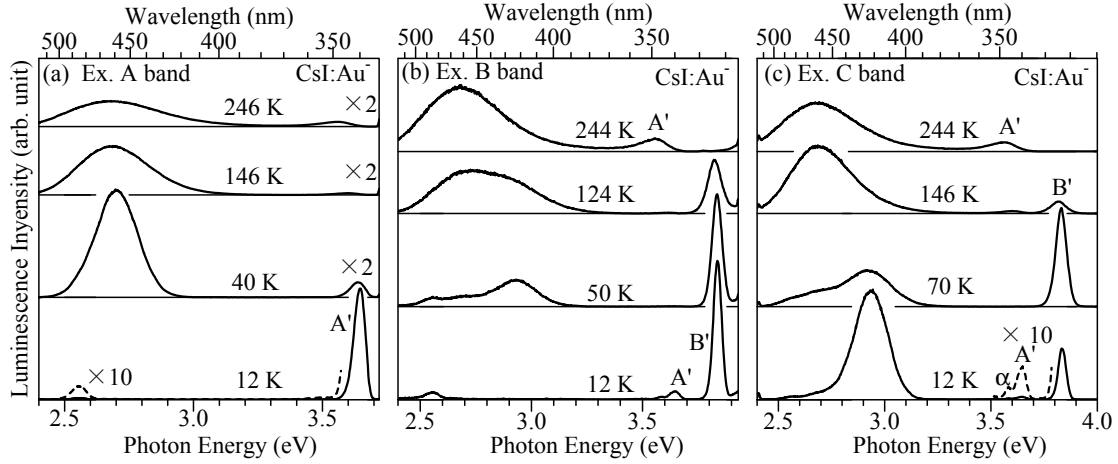
Fig. 6. Temperature dependence of the luminescence spectra of CsI:Au⁻. (a), (b), and (c) correspond to the temperature dependence of the luminescence spectra under excitation at the A, B, and C absorption bands, respectively.

the α luminescence band observed at 3.74 eV diminishes and the A' luminescence band at 3.81 eV appears at 50 K and grows. The complementary relationship between the α and A' luminescence intensities probably comes from the thermally nonradiative transition between the relaxed $^3P_0$ and $^3P_1$ states.

3.4 Temperature dependence of luminescence spectra of CsI:Au⁻

Figures 6(a)-6(c) show the temperature dependence of the luminescence spectra of CsI:Au⁻ under excitation at the A, B, and C absorption bands, respectively. Under excitation at the A absorption band, the A' luminescence band is dominant at low temperatures. As the temperature increases from 25 to 40 K, the A' luminescence intensity decreases. Then, the 2.57 eV luminescence intensity increases with compensation for the decrease in A' luminescence intensity and its peak shifts to 2.73 eV. The A' luminescence band diminishes at about 60 K and again emerges at about 120 K. With increasing temperature from 120 K, the A' luminescence band grows. In the temperature range above 146 K, the visible luminescence band with a maximum at 2.73 eV is dominant. At high temperatures, the visible luminescence band has a band shape with the tail on the higher energy side and can be revolved into the Gaussian shape bands peaking at 2.57 and 2.93 eV.

The temperature dependence of the luminescence bands under excitation at the B and C absorption bands is more complex than that under excitation at the A absorption band, because the four luminescence bands observed in the visible and UV energy region change with temperature. It seems that the four luminescence bands change with temperature while
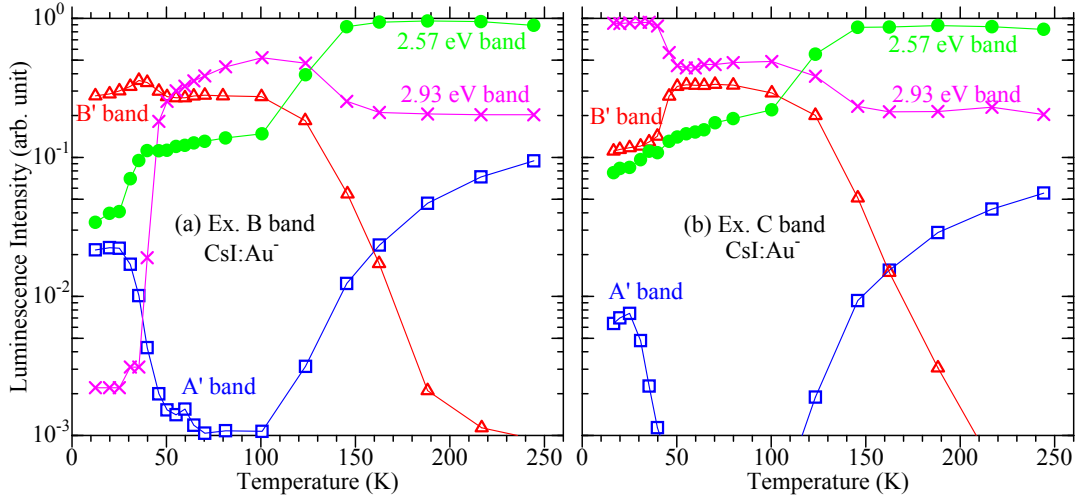
Fig. 7. (Color online) Temperature dependence of the relative intensities of the luminescence bands in CsI:Au⁻ under excitation at the B and C absorption bands. Open squares, open triangles, filled circles, and crosses correspond to the A', B', 2.57 eV, and 2.93 eV luminescence bands, respectively. The vertical axis of the figure is in the logarithmic scale. To facilitate viewing, thin solid lines have been drawn.

complementing each other. The intensities of the luminescence bands under excitation at the B and C absorption bands are plotted as a function of temperature in Figs. 7(a) and 7(b). The luminescence intensities of the 2.57 and 2.93 eV bands at high temperatures were estimated by revolving the visible luminescence band into two Gaussian shape bands. The details of the temperature dependence of the luminescence intensities in CsI:Au⁻ are discussed in the next section.

4. Discussion

4.1 Absorption bands of Tl⁺ -type centers in cesium halides

As mentioned in §1, the Tl⁺ centers in cesium halides exhibit unique absorption bands unlike other $n\mathrm{s}^2$ centers in alkali halides.[22–26] Although the Au⁻ anion has the same $6\mathrm{s}^2$ outermost electron configuration as the Tl⁺ ion, the Au⁻ centers in cesium halides exhibit the A, B, and C absorption bands caused by the intraionic transitions. This fact indicates that the $6\mathrm{s}^2$ outermost electron configuration does not produce the peculiar absorption bands of the cationic $6\mathrm{s}^2$ centers in cesium halides. The difference between the cationic $6\mathrm{s}^2$ centers and the anionic $6\mathrm{s}^2$ centers would be of further help in revealing the cause of the formation of the unusual absorption bands of the cationic $6\mathrm{s}^2$ centers in cesium halides.

The Au⁻ ion is substituted for a halogen ion, while the Tl⁺ ion is located at an alkali ion site, at which the Cs⁺ ion is occupied. The appearance of the A, B, and C absorption bands of

the Au$^-$ centers in cesium halides indicates that the electronic states of the Au$^-$ ion are barely affected by the d states of the Cs$^+$ ion in spite of the nearest-neighbor ion of the Cs$^+$ ion. The difference of the occupying lattice site would be associated with the effect of the d states in the Cs$^+$ ion. The periodicity of the constituent ions might induce the effect of the d states in the Cs$^+$ ion on the electronic states in the cationic 6s^2 centers.

4.2   Origin of visible luminescence bands in Au$^-$ centers in cesium halides

The Au$^-$ centers in cesium halides exhibit other luminescence bands in the visible energy region in addition to the A' and B' luminescence bands. In particular, the visible luminescence bands in CsI:Au$^-$ have a luminescence intensity comparable to the A' and B' luminescence bands.

In the same manner as the Au$^-$ centers in cesium halides, the Tl$^+$ centers in cesium halides also exhibit luminescence bands in the visible energy region in addition to the luminescence bands caused by intraionic transitions.[33–37] In particular, CsI:Tl$^+$ crystals have been widely used as scintillator materials owing to the intense visible luminescence bands. The visible luminescence bands in CsI:Tl$^+$, which consist of two bands peaking at 2.55 and 2.25 eV, are attributed to the self-trapped exciton (STE) perturbed by a Tl$^+$ ion[35–37] and/or the radiative recombination of an electron in a Tl^0 center with a neighboring V$_K$ center.[38,39] Reflecting the origin, the visible luminescence bands in CsI:Tl$^+$ are efficiently induced by excitation at the Tl$^+$-related absorption bands located in the energy region higher than the A absorption band. In contrast, the visible luminescence bands in the Au$^-$ centers in cesium halides are efficiently excited at the energy position of the A and/or C absorption bands. There are no obvious differences in the features of the visible luminescence bands among the samples with various Au$^-$ center concentrations. The findings indicate that the visible luminescence bands arise from the relaxed excited states in the Au$^-$ centers.

The visible luminescence bands in the Au$^-$ centers in cesium halides have larger halfwidth and Stokes shift than the A' and B' luminescence bands. The larger halfwidth and Stokes shift lead us to the idea that the excited states emitting the visible luminescence are associated with the larger lattice relaxation. Here, we tentatively suggest the following origin: the visible luminescence bands are attributed to the radiative transitions from the relaxed excited states of the Au$^-$ ion located at the off-center position in the lattice site, while the A' and B' luminescence bands arise from the relaxed excited states of the Au$^-$ ion located at the on-center position. The on- and off- center lattice configurations of the Au$^-$ centers at the relaxed excited state are schematically drawn in Fig. 8(a). Such an off-center displacement of
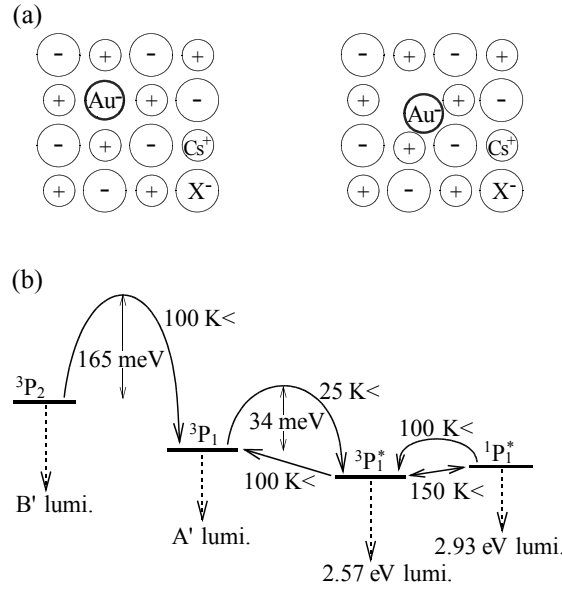
Fig. 8. (a) Schematic lattice configurations of the Au$^-$ ions located at the on-center and off-center positions in the lattice site. (b) Energy levels of the relaxed $^3P_2$, $^3P_1$, $^3P_1^*$, and $^1P_1^*$ states shown to explain the luminescence properties of CsI:Au$^-$. Dashed down arrows indicate radiative processes from the relaxed excited states. Obliquely up arrows indicate a thermal distribution from lower energy levels. Upward curved arrows indicate thermally activated nonradiative transitions through a barrier.

the ns^2-like ions in alkali halide crystals has been reported for the relaxed excited states of the Ga$^+$ and In$^+$ centers.[9,40,41]

4.3 Nonradiative transition processes among excited states in CsI:Au$^-$

In the Au$^-$ center in CsI, the A', B', 2.57, and 2.93 eV luminescence bands change with temperature while complementing each other. The complementary temperature dependence comes from thermally activated nonradiative transitions among the relaxed excited states. Since the 2.57 and 2.93 eV luminescence bands in CsI:Au$^-$ are efficiently excited in the energy region at the A and C absorption bands, respectively, we describe the initial states exhibiting the 2.57 and 2.93 eV luminescence bands as $^3P_1^*$ and $^1P_1^*$, respectively. To explain the complementary temperature dependence, we consider the energy levels and nonradiative transitions among the relaxed excited states, which are schematically shown in Fig. 8(b).

Although the plots of the temperature dependence of the 2.57 eV and A' luminescence intensities under excitation at the A absorption band are not shown, the intensities of the 2.57 eV and A' luminescence bands in CsI:Au$^-$ are obviously complementary to each other in the temperature range between 25 and 40 K. The complementary change between the 2.57 eV and A' luminescence band arises from the thermally activated nonradiative transition from

the relaxed $^3P_1$ to $^3P_1^*$ states. From the decrease in A' luminescence intensity with increasing temperature, the activated energy for the nonradiative transition from the relaxed $^3P_1$ to $^3P_1^*$ states is estimated to be about 34 meV. The intensity of the A' luminescence band increases with increasing temperature from 100 K even under excitation at the A absorption bands. Since the relaxed $^3P_1$ state is located above the relaxed $^3P_1^*$ state, the thermal redistribution from the relaxed $^3P_1^*$ to $^3P_1$ states would occur in the temperature range above 100 K.

The temperature dependence of the luminescence intensities under excitation at the B and C absorption bands is complex, especially in the temperature range below 50 K. As shown in Fig. 7, the complementary change between the B' and 2.93 eV luminescence intensities in the temperature range from 40 to 50 K is very different between excitations at the B and C absorption bands. The temperature dependence of the luminescence intensities cannot be explained by the thermally activated nonradiative transitions among the relaxed $^3P_1$, $^3P_2$, $^3P_1^*$, and $^1P_1^*$ states. To explain this temperature dependence, we must consider the following relaxation processes from the higher excited states to the relaxed $^3P_1$, $^3P_2$, $^3P_1^*$, and $^1P_1^*$ states, which are not drawn in Fig. 8(b).

The excitation at the B absorption band induces the transitions to the excited $^3P_2$ state. At low temperatures, the relaxation process from the excited $^3P_2$ state to the relaxed $^3P_2$ state mainly occurs. Around 40 K, the relaxation pathway from the excited $^3P_2$ state to the relaxed $^1P_1^*$ state is opened and the relaxation process to the relaxed $^3P_2$ state is inhibited. Under excitation at the C absorption band, on the other hand, the $^1P_1$ state is excited. Then, the relaxation process from the excited $^1P_1$ state to the relaxed $^1P_1^*$ state preferentially occurs below 40 K. Around 40 K, the relaxation process from the excited $^1P_1$ state to the relaxed $^3P_2$ state begin to occur and the relaxation process to the relaxed $^1P_1^*$ state is inhibited.

In the temperature region above 100 K, the temperature dependence of the luminescence intensities under excitation at the B band is the same as that under excitation at the C band. The behavior can be explained on the basis of the nonradiative transitions among the relaxed $^3P_1$, $^3P_2$, $^3P_1^*$, and $^1P_1^*$ states. The decrease in B' luminescence intensity with increasing temperature from 100 K comes from the thermally activated nonradiative transition from the $^3P_2$ to $^3P_1$ states. From the decrease in B' luminescence intensity, the activated energy for the nonradiative transition from the $^3P_2$ to $^3P_1$ states is estimated to be about 165 meV. Similarly to the case of excitation at the A absorption band, the A' luminescence intensity increases with increasing temperature from 100 K. The increase in A' luminescence intensity arises from the thermal redistribution from the $^3P_1^*$ to $^3P_1$ states, as mentioned above. The increase in 2.57 eV luminescence intensity and the decrease in 2.93 eV luminescence intensity in the

temperature range between 100 and 150 K are derived from the thermally activated nonradiative transition from the $^1P_1^*$ to $^3P_1^*$ states. In the temperature range above 150 K, the intensity ratio between the 2.57 and 2.93 eV luminescence bands is constant, indicating that the $^3P_1^*$ and $^1P_1^*$ states are at thermal equilibrium with each other.

The luminescence properties of the Au$^-$ center in cesium halides are complex owing to the presence of the visible luminescence bands. In order to clarify the nonradiative transition processes and the origin of the visible luminescence bands in CsI:Au$^-$ and CsBr:Au$^-$ crystals, precise measurements of the decay kinetics and polarization properties of the luminescence bands are planned.

5. Conclusions

The temperature dependence of the absorption and luminescence spectra has been investigated for the Au$^-$ centers in CsBr and CsI single crystals with the CsCl structure. The A, B, C, and D absorption bands caused by the intraionic transitions in the Au$^-$ ion are observed at 12 K. When the samples are irradiated by light with energies corresponding to the absorption bands, the A' and B' luminescence bands caused by the radiative transitions from the relaxed excited states of $^3P_1$ and $^3P_2$ appear with a small Stokes shift, reflecting a weak electron-phonon interaction. In addition to the A' and B' luminescence bands, other luminescence bands are observed in the visible energy region. The visible luminescence bands have excitation bands at the energy positions of the A and C absorption bands. From the analogy with the lattice configurations of STEs in alkali halides, the origins of the visible luminescence bands are tentatively assigned to the radiative transitions from the relaxed excited $^1P_1$ and $^3P_1$ states in the Au$^-$ centers having the off-center lattice configuration. The A', B', and visible luminescence bands change with temperature while complementing each other. The experimental results can be explained on the basis of the thermally activated nonradiative transitions among the relaxed excited states.

Acknowledgment

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