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Energy transfer from CsI host lattice to Ag⁻ centers in CsI:Ag⁻ crystals

Satoru Nagata [a], Taketoshi Kawai [a,*], Takeshi Hirai [b]

[a] Department of Physical Science, Graduate School of Science, Osaka Prefecture University, Gakuen-cho 1-1, Naka-ku, Sakai, Osaka 599-8531, Japan
[b] Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University, Noji Higashi 1-1-1, Kusatsu, Shiga 525-8577, Japan

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ABSTRACT

Luminescence properties of CsI single crystals doped with Ag⁻ ions have been investigated under excitation in the energy range from 3 to 12 eV. When the crystals are excited at photon energy around 3.79 eV corresponding to the C absorption band of Ag⁻ centers, the A′ and C′ luminescence bands of the Ag⁻ center are observed at 2.53 and 3.45 eV, respectively. Under excitation above the band gap energy of CsI (6.1 eV), the luminescence bands originating from the on- and off-center type self-trapped excitons (STEs) of CsI are observed at 3.60 and 4.30 eV, respectively, in addition to the A′ and C′ luminescence bands. The excitation spectra for the A′ and C′ luminescence in the energy region above the band gap energy are nearly the same as that for the off-center STE luminescence. The temperature dependence of the A′ luminescence intensity is similar to that of the off-center STE luminescence intensity in the luminescence spectra under the excitation above the band gap energy. Furthermore, the temporal behavior of the C′ luminescence band resembles that of the off-center STE luminescence band. On the basis of the characteristics of the A′, C′ and off-center STE luminescence bands, the energy transfer mechanism from the CsI host crystals to the Ag⁻ impurity centers in the CsI:Ag⁻ crystals is discussed.

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1. Introduction

Energy transfer process in alkali halide crystals widely used as scintillation crystals has been extensively investigated, since it plays a crucial role in the scintillation process [1–6]. When the alkali halide crystals are irradiated by photons with energy exceeding the band gap energy, free electrons and holes are created in the conduction and valence bands, respectively. The free electrons and holes are immediately self-trapped owing to the strong electron–phonon interaction, and hole trapped centers (V_K centers) and/or self-trapped excitons (STEs) are formed in the crystals [7]. The self-trapped holes ultimately undergo radiative recombination with the electrons.

In the case of alkali halide crystals containing Tl⁺-type ions, which have the ns^2 electronic configuration in their ground state [8–11], the excitation energy can transfer from the alkali halide host crystals to the Tl⁺-type impurity ions through the migration of free excitons. The thermally activated hopping motion of the V_K centers and/or STEs can also give rise to the excitation energy transfer to the Tl⁺-type ions [1–3,12–16]. Furthermore, the reabsorption of emission light by the Tl⁺-type ions may follow the emission due to the radiative recombination of STEs, resulting in the excitation energy transfer to the Tl⁺-type ions. It is of importance to clarify the mechanisms of energy transfer from host

crystals to impurity ions in alkali halide crystals doped with Tl⁺-type ions from a fundamental and applied physics point of view.

In this paper, we have studied the energy transfer from CsI host crystals to Ag⁻ impurity centers in CsI:Ag⁻ crystals. The CsI crystals are very popular as host crystals for γ- and X-ray scintillators. The Ag⁻ center is one of the Tl⁺-type centers [17–23]. The CsI:Ag⁻ crystals exhibit simple absorption and luminescence characteristics in comparison to CsI:Tl⁺ crystals practically employed as the γ- and X-ray scintillation crystals. The simple spectral properties of the Ag⁻ center help us to discuss the mechanisms of the energy transfer from the CsI host crystal to the Ag⁻ centers.

2. Experimental method

The addition of Ag⁺ ions into pure CsI single crystals (Union Material Inc.) was performed by a diffusion reaction of AgI powders (Nacalai Tesque Inc.) with the crystals heated at about 500 °C. The conversion from the Ag⁺ to Ag⁻ ions in the crystals was achieved by an electrolytic coloration technique. The crystals were cut and polished to about 0.5 mm thick. In order to remove F centers and isolate the Ag⁻ centers, the samples were wrapped in an aluminum foil and heated up to about 500 °C for about 30 s followed by fast cooling at RT.

The optical measurements were performed at the BL-1B line of UVSOR (Institute for Molecular Science, Okazaki, Japan). The light beam from 750 MeV electron storage ring of synchrotron radiation was monochromatized through a 1 m Seya–Namioka type

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* Corresponding author. Tel.: +81 72 254 9196; fax: +81 72 254 9931.
E-mail address: buri@p.s.osakafu-u.ac.jp (T. Kawai).

monochromator. The samples were mounted on a cold stage of a liquid helium-flow type cryostat and cooled down to 6 K. The luminescence and excitation spectra were measured by using a monochromator (Acton Spectra Pro-300i) together with a LN-cooled CCD detector (Roper Scientific LN/CCD-100EB-GI) and a photomultiplier (Hamamatsu R4220), respectively. The absorption spectra were measured by using another photomultiplier (Hamamatsu R105) coated with a sodium salicylate phosphor.

The measurements of the time-resolved luminescence spectra were made by using an ArF excimer laser (Lambda Physik, COMPex 102) with the oscillation wavelength of 193 nm and pulse duration of about 15 ns and a detection system (ORIEL Instruments, INSTA-SPEC™ V) consisting of a monochromator (MS257TM) and an intensified CCD detector (Model 77193) in our laboratory. The samples were mounted on a copper cold stage connected with a cryogenic refrigerator (Iwatani Gas Co. Ltd., Cryomini D type).

3. Experimental results

Fig. 1a shows an absorption spectrum of Ag⁻ centers doped in a CsI crystal at 6 K. A marked absorption band peaking at 3.79 eV, which is called the C absorption band, is attributed to the transition from the $^1A_{1g}$ ground state to the $^1T_{1u}$ excited state in the Ag⁻ center [17,20]. The concentration of the Ag⁻ center in the CsI crystal is estimated to be at about 3×10^{17} number/cm³ by using Smakula's equation from the C absorption intensity [24,25].

Fig. 1b shows luminescence spectra of the CsI:Ag⁻ crystal under excitation at 3.82 and 6.42 eV at 6 K. When the CsI:Ag⁻ crystal is excited at 3.82 eV, there appear two luminescence bands peaking at 2.53 and 3.45 eV. The 2.53 and 3.45 eV luminescence bands are attributed to the radiative transitions from the relaxed excited states of $^3T_{1u}$ and $^1T_{1u}$ in the Ag⁻ center, which are called the A′ and C′ luminescence bands, respectively [20]. As shown by the thick solid line in Fig. 1b, on the other hand, broad luminescence bands peaking at 3.6 and 4.2 eV are observed in addition to the A′ luminescence band under excitation at 6.42 eV which is higher than the band-gap energy of CsI. The 3.6 and 4.2 eV luminescence bands are attributed to the off- and on-center type self-trapped excitons
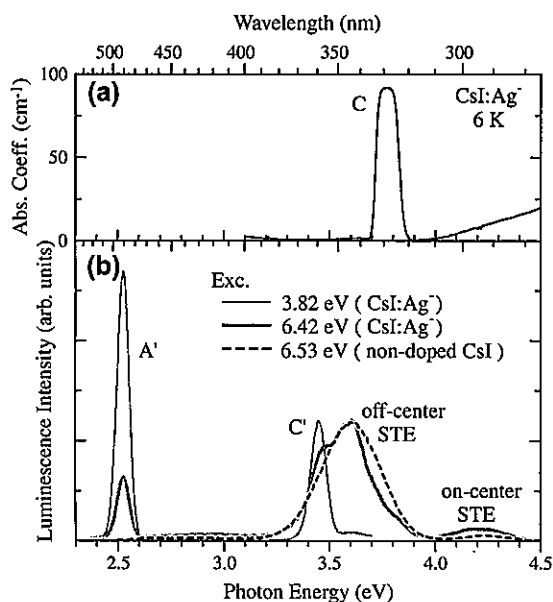
(STEs) in the CsI crystals, respectively [7,26]. Although the STE luminescence band usually has a standard Gaussian shape, the off-center STE luminescence band of the CsI:Ag⁻ crystal has a small shoulder at 3.45 eV and a slight dent around 3.70 eV. The small shoulder at 3.45 eV comes from the C′ luminescence band due to the Ag⁻ center. The dent at 3.70 eV in the off-center STE luminescence band is attributed to the reabsorption by the C absorption band peaking at 3.79 eV.

Fig. 2 shows excitation spectra for the A′, C′, and off-center STE luminescence bands in the energy range from 3 to 12 eV. The off-center STE luminescence band is efficiently excited in the energy region above the fundamental absorption edge of the CsI crystals (6.1 eV). The excitation spectra for the A′ and C′ luminescence bands exhibit a pronounced peak at 3.79 eV, which corresponds to the C absorption band. What has to be noticed is that the excitation spectra for the A′ and C′ luminescence bands have the similar excitation spectra to the off-center STE luminescence in the energy range above the absorption edge of the CsI crystals.

Fig. 3a shows the temperature dependence of the luminescence spectra of the CsI:Ag⁻ crystal under excitation at 3.79 eV, which corresponds to the peak energy of the C absorption band. The A′ and C′ luminescence bands due to the Ag⁻ center are observed at low temperatures. As the temperature rises, the C′ luminescence band rapidly decreases and disappears at 30 K. On the other hand, the A′ luminescence band increases with increasing temperature from 6 K and has the maximum in intensity at 20 K. Although the A′ luminescence band becomes broad with increasing temperature from 100 K, the A′ luminescence band can be observed even at 300 K.

Fig. 3b shows the temperature dependence of the luminescence spectra of the CsI:Ag⁻ crystal under excitation at 6.42 eV, which corresponds to the band-to-band excitation of CsI. The shoulder structure at 3.45 eV in the off-center STE luminescence band cannot be seen at 20 K, suggesting the quenching of the C′ luminescence band above 20 K. The dent structure around 3.70 eV, which is attributed to the reabsorption by the C absorption band, becomes observable at high temperatures. Under excitation at 6.42 eV, the A′ luminescence band disappears at 130 K, while a broad luminescence band peaking at 2.85 eV appears above 100 K. The 2.85 eV luminescence band is considered to be related with Na impurity ions from the peak position [27,28]. A small fraction of the Na ions might be included in the pure CsI single crystals purchased.

The temperature dependences of the luminescence intensities of the A′, C′ and STE bands in the CsI:Ag⁻ crystal are plotted as a
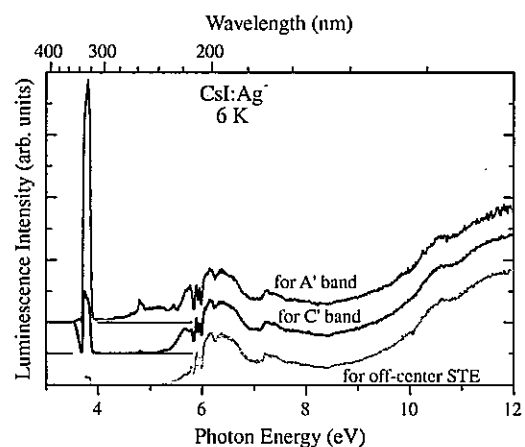

Fig. 1. (a) Absorption and (b) luminescence spectra of a CsI:Ag⁻ crystal under excitation at 3.82 eV (thin solid line) and 6.42 eV (thick solid line). For reference, the luminescence spectrum of non-doped CsI crystals is shown by broken line.

Fig. 2. Excitation spectra for the A′, C′, and off-center STE luminescence bands of the CsI:Ag⁻ crystal at 6 K.
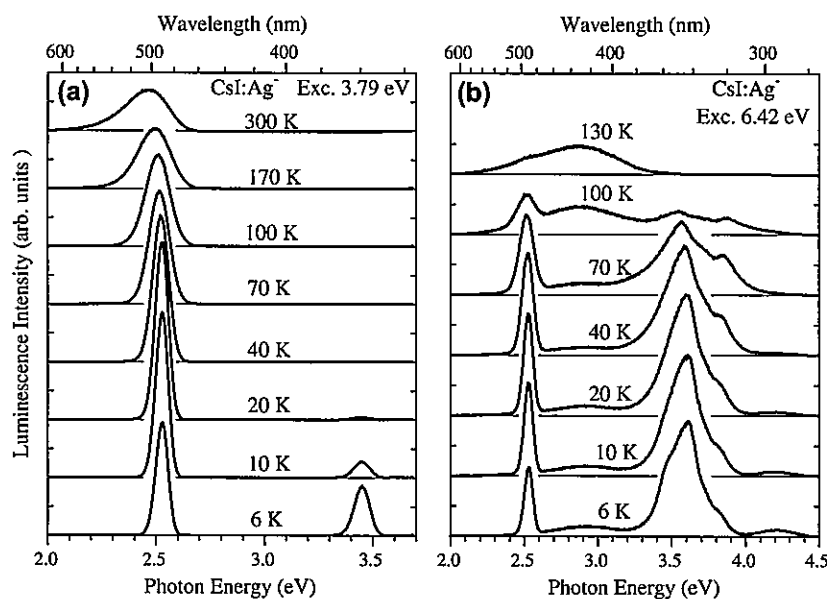
Fig. 3. Temperature dependences of the luminescence spectra of the CsI:Ag⁻ crystal under excitation at 3.79 eV (a) and 6.42 eV (b).
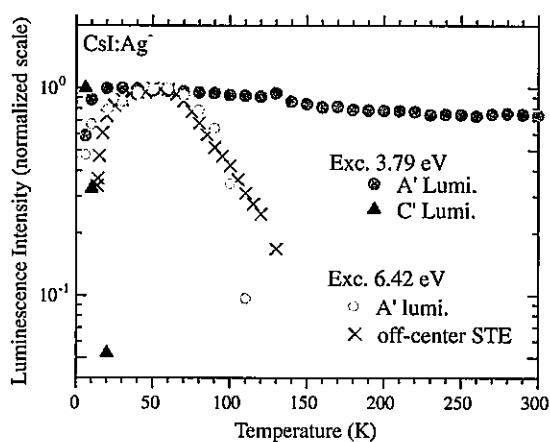

Fig. 4. Temperature dependences of the A', C' and STE luminescence intensities of the CsI:Ag⁻ crystal. Filled circles and triangles correspond to the A' and C' luminescence bands under excitation at 3.79 eV, respectively. Open circles and crosses correspond to the A' and off-center STE luminescence band under excitation at 6.42 eV, respectively.

Fig. 5. Time-resolved luminescence spectra of the CsI:Ag⁻ crystal measured by using the ArF excimer laser at 12 K.

function of temperature in Fig. 4. Under excitation at 3.79 eV, the luminescence intensity of the C' band decreases with increasing temperature from 6 to 20 K. The increase in the intensity of the A' luminescence band is accompanied by the decrease in that of the C' luminescence band. The complementary change between the A' and C' luminescence bands arises from the thermally activated nonradiative transition from the relaxed $^1T_{1u}$ to $^3T_{1u}$ states [22,23]. The A' luminescence intensity hardly changes in the temperature range above 20 K. The result implies that the thermally activated nonradiative transition from the $^3T_{1u}$ state to another state hardly occurs.

Under excitation at 6.42 eV, the A' luminescence intensity increases with increasing temperature from 6 to 60 K, and decreases with increasing temperature from 60 K. The temperature dependence of the A' luminescence intensity is similar to that of the off-center STE luminescence intensity. The similar temperature dependences of the intensities in the A' and off-center STE luminescence bands indicate a close relationship between the two luminescence bands.
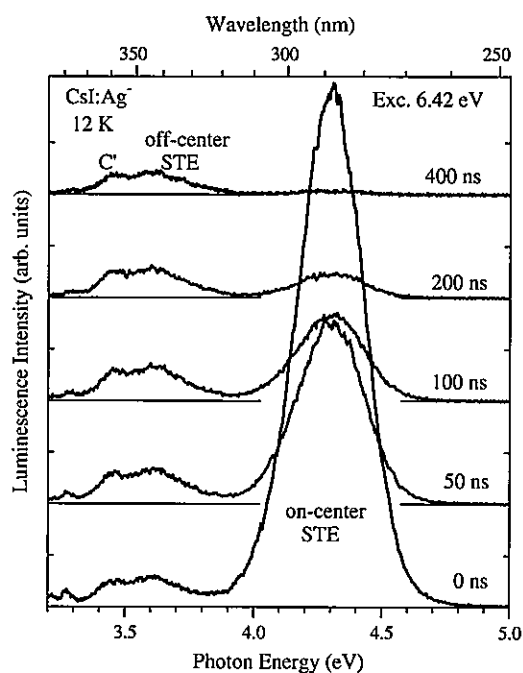
Fig. 5 shows time-resolved luminescence spectra measured by using the ArF excimer laser (oscillation wavelength: 193 nm, pulse duration: ~15 ns). Three luminescence bands peaking at 3.45, 3.60, and 4.30 eV correspond to the C' luminescence band, the off- and on-center STE luminescence bands, respectively. The on-center STE luminescence band at 4.30 eV is predominant in the spectra of 0–100 ns, but disappears in the spectrum of 400 ns. The decay time constant for the on-center STE luminescence band is estimated to be 90 ns, which is coincident with that of the radiative transition from the triplet states of the on-center STEs in the CsI crystals [26]. The C' luminescence band and the off-center STE luminescence band are almost unchanged in the spectra of 0–400 ns.

4. Discussion

Since the CsI crystals have the large absorption coefficients beyond 10^5 cm^{-1} in the energy region above the band gap energy, the penetration depth of the incident light is estimated to be only a few hundred nm. Accordingly, free electrons and holes are mainly created nearby the crystal surface under the band-to-band excitation of CsI. The Ag$^-$ centers are uniformly distributed over the interior of host crystals; thus, the number of the Ag$^-$ centers directly excited under the band-to-band excitation should be extremely small as compared with that under excitation at the C absorption band of the Ag$^-$ center. Nevertheless, the A' and C' luminescence intensities under the band-to-band excitation are comparable to those under excitation at the C absorption band, as shown in Fig. 2. This fact indicates the existence of the efficient energy transfer from the CsI host crystal to the Ag$^-$ centers at low temperatures.

In undoped CsI and NaI crystals, the thermally activated hopping motion of the STEs often plays an important role in the energy transfer processes [12,26,27,29]. When the hopping motion of the STEs is enhanced with increasing temperature, the STEs can encounter the impurity ions and transfer their energy to the impurity ions before recombining radiatively or nonradiatively. Then, the luminescence band related to the impurity ions grows and the STE luminescence band diminishes.

In the CsI:Ag$^-$ crystal, the off-center STE luminescence intensity decreases with increasing temperature from 60 K, as shown in Fig. 4. Similarly to the case of the off-center STE luminescence intensity, the A' luminescence intensity also decreases with increasing temperature from 60 K. The fact suggests that the hopping motion of the STEs does not contribute to the energy transfer to the Ag$^-$ centers. Furthermore, the thermally activated hopping motion does not occur at low temperatures. We have to consider another mechanism for the energy transfer process from the CsI host crystal to the Ag$^-$ centers in the CsI:Ag$^-$ crystal.

The excitation energy transfer is related to the reabsorption of off-center STE luminescence by the C absorption of the Ag$^-$ center. The dent structure in the off-center STE luminescence band shown in Fig. 1 is attributed to the reabsorption by the C absorption band, suggesting the Ag$^-$ centers are excited by the emission light arising from the radiative recombination of the off-center STEs. The similar temperature dependences of the A' and off-center STE luminescence bands also suggest the excitation of the Ag$^-$ centers by the off-center STE luminescence. From these results, we conclude that emission reabsorption mechanism plays an important role in the energy transfer process from the CsI host crystal to the Ag$^-$ centers.

The temporal behavior of the C' luminescence band shown in Fig. 5 can be interpreted in terms of the excitation energy transfer due to the emission reabsorption. In general, the radiative decay times of the C' luminescence bands of the Ag$^-$ centers doped in alkali halide crystals is about 1 ns at low temperatures under excitation at the C absorption band reflecting the singlet nature of the relaxed $^1T_{1u}$ state [21–23]. In the CsI:Ag$^-$ crystal under the band-to-band excitation, however, the C' luminescence band can be observed even in the spectrum of 400 ns shown in Fig. 5, indicating the apparent decay time of the C' luminescence band is much longer than 1 ns. Furthermore, the decay time of the C' luminescence band is very likely to be consistent with that of the off-center STE luminescence band. The results strongly suggest that, while the off-center STEs radiatively recombine, the Ag$^-$ centers are excited by the emission light.

5. Conclusion

We have measured the absorption, luminescence, excitation, and time-resolved luminescence spectra of the CsI crystal doped with Ag$^-$ ions. Under the band-to-band excitation of the CsI host crystal, the off-center STE luminescence band observed around 3.6 eV has a shoulder structure at 3.45 eV and a dent structure at 3.70 eV. The shoulder and dent structures come from the C' luminescence located at 3.45 eV and the reabsorption by the C absorption band peaking at 3.79 eV, respectively. The fact implies that the Ag$^-$ centers are excited by the off-center STE luminescence through the reabsorption by the C absorption band. At low temperatures, the A', C', and off-center STE luminescence bands have the similar excitation spectra in the energy region above the band gap of CsI. Furthermore, the C' luminescence band in the CsI:Ag$^-$ crystal under the band-to-band excitation is observed together with the off-center STE luminescence band even in the time region beyond 100 ns after excitation. These results can be explained by the energy transfer from the CsI host crystal to the Ag$^-$ centers through the reabsorption of the off-center STE luminescence by the C absorption band.

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