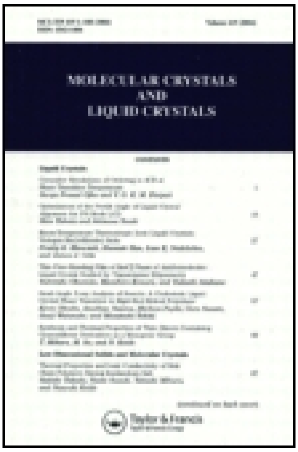

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Relaxation Process of CT Exciton State in a One-Dimensional MX-Chain Compound NiBr(chxn) 2]Br 2

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Relaxation Process of CT Exciton State in a One-Dimensional MX-Chain Compound $[\mathrm{NiBr}(chxn)_2]\mathrm{Br}_2$

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Luminescence spectroscopy measurements were performed in a one-dimensional halogen-bridged transition-metal compound $[\mathrm{NiBr}(chxn)_2]\mathrm{Br}_2$ (*chxn*: 1*R*,2*R*-cyclohexanediamine) and its mixed-metal compound $[\mathrm{Ni}_{1\text{-}x}\mathrm{Pd}_x\mathrm{Br}(chxn)_2]\mathrm{Br}_2$ with x = 0.005, 0.05, 0.33. The broad peaks were observed at 1.3 and 1.4 eV for $[\mathrm{NiBr}(chxn)_2]\mathrm{Br}_2$, which are attributed to a relaxation of LMCT exciton state and a hot luminescence, respectively. No Stokes shift of the luminescence at 1.3 eV was observed, which shows the electron-lattice interaction (*S*) is weak in this system. From the temperature dependence of luminescence spectra, it was clarified that the relaxation process is continuously changed from luminescence to thermal relaxation. The luminescence peak at 1.3 eV is remarkably quenched with increase of x for $[\mathrm{Ni}_{1\text{-}x}\mathrm{Pd}_x\mathrm{Br}(chxn)_2]\mathrm{Br}_2$, implying that the LMCT exciton is trapped to in-gap states caused by doped Pd^{3+}.

Keywords MX chain; luminescence; charge-transfer exciton; mixed valence

INTRODUCTION

A series of one-dimensional halogen-bridged(X) transition-metal(M) complexes (MX-chains) have been studied as a Peierls distorted system with a strong electron-lattice interaction resulting in mixed-valence state. Recently, a new type of MX-chain complexes [NiX(*chxn*)$_2$]X$_2$ (*chxn*: 1*R*,2*R*-cyclohexanediamine; X: Cl, Br) have been shown to crystallize with no Peierls distortion implying the formation of $S = 1/2$ spin chain of Ni^{III}. From an optical conductivity for [NiBr(*chxn*)$_2$]Br$_2$, an energy gap of this complex was measured to be about 1.3 eV[1], and the on-site Coulomb repulsion (*U*) was determined to be 5 eV from X-ray photoelectron and Auger spectroscopies[2]. Since the optical energy gap was much smaller than *U*, this material is recognized as a charge-transfer insulator. Thus, the peak at 1.3 eV is attributed to a charge-transfer transition from bridging-halogen to metal (LMCT) [2]. Although relaxation processes in Peierls-distorted (mixed-valence) MX-chain compounds have been extensively studied[3-8], the processes in [NiX(*chxn*)$_2$]X$_2$ are not clarified. In this paper, we report on luminescence properties of the non-Peierls MX-chain system [NiBr(*chxn*)$_2$]Br$_2$.

EXPERIMENTAL

Single crystals of [NiBr(*chxn*)$_2$]Br$_2$ were prepared by a slow diffusion of Br$_2$ vapor into a solution [Ni(*chxn*)$_2$]Br$_2$ dissolved in methanol. Single crystals of a mixed-metal MX-chain system [Ni$_{1-x}$Pd$_x$Br(*chxn*)$_2$]Br$_2$ were prepared by an electrochemical oxidation method described elsewhere[9]. The concentration of metals in measured specimens was determined by ICP emission spectrometry. The luminescence spectroscopy measurements were performed using a DIOLOR-JOBINYVON-SPEX spectrometer with He-Ne (1.96 eV) and Ar ion (2.41 eV) lasers as excitation light sources. Incident laser was polarized parallel to the chain axis (***E*** // *b*).

RESULTS AND DISCUSSION

Figure 1 shows the luminescence spectra of [NiBr(*chxn*)$_2$]Br$_2$ at 2 K for the excitation energy of 1.96 and 2.41 eV. Large and small broad peaks were observed at 1.3 and 1.4 eV, respectively. It is reported that an intense band was observed at 1.3 eV in the optical conductivity spectrum[2], being accounted to be a LMCT transition (Br$^-$, Ni^{3+} → Br^0, Ni^{2+}). The luminescence peak observed at 1.3 eV is, therefore, considered to be a relaxation of LMCT exciton state (Br^0, Ni^{2+} → Br^-, Ni^{3+}). This luminescence exhibits no or little Stokes shift, showing that the LMCT exciton is not easy to be relaxed into a self-trapped state. This is a good contrast to a relaxation process of the CT exciton state (M^{3+}, $M^{3+} \rightarrow M^{4+}$, M^{2+}) in Peierls-distorted MX-chain system of M = Pd, Pt. These materials show large Stokes shifts due to the strong electron-lattice interaction because bridging halogen ion X^- are quite sensitive to the charge of metal ions. On the other hand in $[NiBr(chxn)_2]Br_2$, the bridging bromine, which is neutral (Br^0) when the LMCT occurs, is insensitive to the charge at Ni ions, so that the electron-lattice interaction(S) of this system is small. The very small S in $[NiBr(chxn)_2]Br_2$ supports the validity of description of electron state in this system with extended-Hubburd model[10]. The small broad peak at 1.4 eV would be attributed to a hot luminescence.

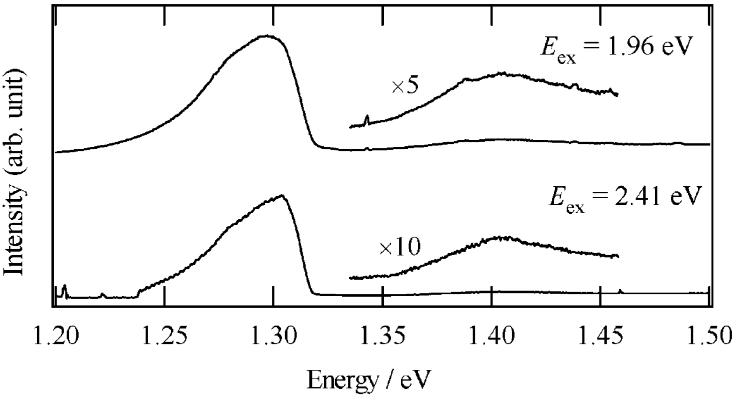

FIGURE 1 Luminescence spectra of $[NiBr(chxn)_2]Br_2$ at 2 K for the excitation energy of 1.96 and 2.41 eV.

Figure 2 shows the temperature dependence of luminescence spectra with excitation energy E_{ex} = 1.96 eV. The peaks at 1.3 and 1.4 eV are gradually disappeared with temperature. This shows that the deactivation process is continuously changed from luminescence to thermal relaxation. The peak at 1.3 eV slightly shifts to low energy with temperature. This slight shift might be accounted as follows. The Ni-Br distance is expected to become longer with temperature, resulting in a decrease of the separation of Br^-

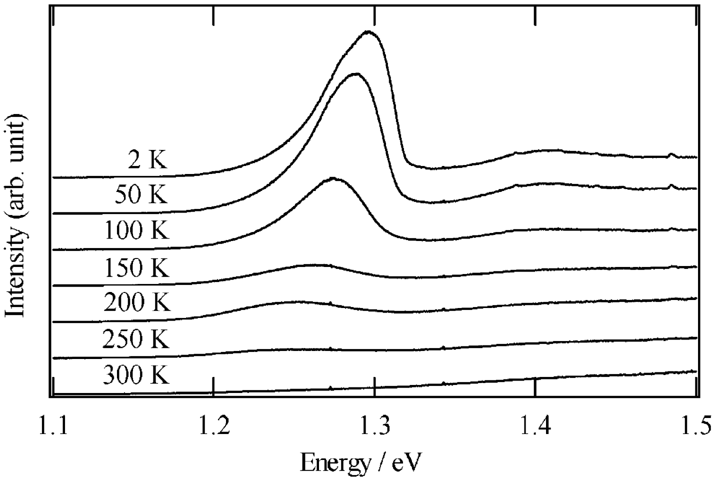

FIGURE 2 Temperature dependence of luminescence spectra in $[NiBr(chxn)_2]Br_2$ with excitation energy $E_{ex} = 1.96$ eV.

$3p_z$ and Ni^{3+} $3d_z{}^2$ orbitals.

The luminescence spectra of mixed-metal complexes $[Ni_{1-x}Pd_xBr(\mathit{chxn})_2]Br_2$ (x = 0.005, 0.05, 0.33) at 2 K for the excitation energy of 1.96 eV are shown in Figure 3. The luminescence at 1.3 eV is remarkably quenched with increase of x. It is reported that the Pd ion in $[Ni_{1-x}Pd_xBr(\mathit{chxn})_2]Br_2$ exists as Pd^{3+} in the range of $0 < x < 0.6$ [11,12].

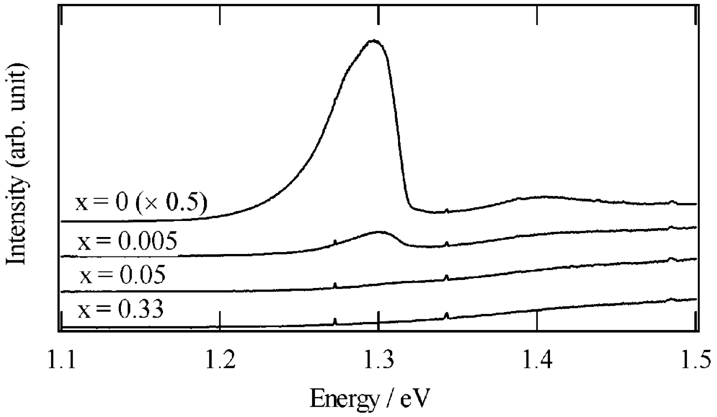

FIGURE 3 Luminescence spectra in $[Ni_{1-x}Pd_xBr(chxn)_2]Br_2$ with x = 0, 0.005, 0.05, 0.33 for the excitation energy of 1.96 eV at 2 K.

Therefore, the impurity level of Pd^{3+} is considered to quench the luminescence at 1.3 eV. From optical conductivity measurements in $[Ni_{1-x}Pd_xBr(\mathit{chxn})_2]Br_2$[13], broad LMCT band shifts to the low-energy side with increasing x. This result implies that the energy level of d_z^2 orbital of Pd^{3+} is located between the $3p_z$ band of Br^- and upper Hubburd band (UHB) of Ni^{3+}. An expected schematic electronic structure is shown in Figure 4. The disappearance of luminescence can be accounted as follows. The LMCT exciton is trapped to the in-gap states, formed by $4d_z^2$ orbitals of Pd^{3+}.

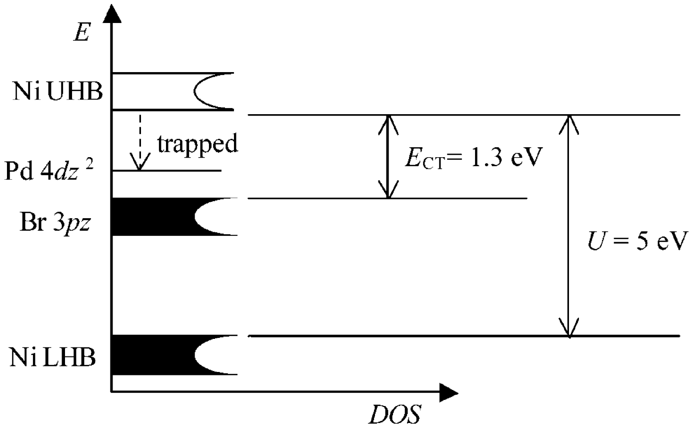

FIGURE 4 Schematic electronic structure for $[Ni_{1-x}Pd_xBr(chxn)_2]Br_2$ (x ál).

CONCLUSION

We have investigated the relaxation process of $[NiBr(\mathit{chxn})_2]Br_2$ and $[Ni_{1-x}Pd_xBr(\mathit{chxn})_2]Br_2$ by means of luminescence spectroscopy. In $[NiBr(\mathit{chxn})_2]Br_2$, LMCT exciton state is not deactivate *via* self-trap exciton state, and this process is changed from luminescence to thermal relaxation with temperature. On the other hand in $[Ni_{1-x}Pd_xBr(\mathit{chxn})_2]Br_2$ (x = 0.005, 0.05, 0.33), the luminescence is almost quenched even at 2 K, because the LMCT exciton state is trapped to the in-gap states, which is formed by $4d_z^2$ orbitals of Pd^{3+}.

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References

[1.] H. Okamoto, K. Toriumi, T. Mitani, and M. Yamashita, *Phys. Rev.* **B42**, 10381(1990).
[2.] H. Okamoto, Y. Shimada, Y. Oka, A. Chainani, T. Takahashi, H. Kitagawa, T. Mitani, K. Toriumi, K. Inoue, T. Manabe, and M. Yamashita, *Phys. Rev.* **B54**, 8438(1996).
[3.] Y. Wada, T. Mitani, M. Yamashita, and T. Koda, *J. Phys. Soc. Jpn.*, **54**, 3143(1985).
[4.] Y. Wada, N. Matsushita, and M. Yamashita, *Mol. Cryst. Liq. Cryst.*, **216**, 175(1992).
[5.] H. Okamoto, T. Mitani, *Prog. Theor. Phys. Supp.*, **113**, 191(1993).
[6.] H. Okamoto, Y. Oka, T. Mitani, K. Toriumi, M. Yamashita, *Mol. Cryst. Liq. Cryst.*, **256**, 161(1994).
[7.] H. Okamoto, Y. Kaga, Y. Shimada, Y. Oka, Y. Iwasa, T. Mitani, and Yamashita, *Phys. Rev. Lett.*, **80**, 861(1998).
[8.] H. Okamoto, M. Yamashita, *Bull. Chem. Soc. Jpn.*, **71**, 2023(1998).
[9.] T. Manabe, M. Yamashita, T. Kawashima, H. Okamoto, H. Kitagawa, T. Mitani, K. Toriumi, H. Miyamae, K. Inoue, and K. Yakushi, *Proc. SPIE*, **3145**, 106(1998).
[10.] N. Tomita, K. Nasu, *Phys. Rev.* **B56**, 3779(1997).
[11.] K. Marumoto, H. Tanaka, S. Kuroda, T. Manabe, and M. Yamashita,*Phys. Rev.* **B60**, 7699(1999).
[12.] N. Kimura, M. Kano, T. Manabe, M. Yamashita, and R. Ikeda, *Synth. Met.*, **120**, 777(2001).
[13.] M. Yamashita, T. Ishii, H. Matsuzaka, T. Manabe, T. Kawashima, H. Okamoto, H. Kitagawa, T. Mitani, K. Marumoto, and S. Kuroda, *Inorg. Chem.*, **38**, 5124(1999).