Ultrafast optical responses in one-dimensional Mott insulators of halogen-bridged Ni compounds

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Abstract. Halogen-bridged nickel compounds have attracted much attention because they show large optical nonlinearity and photinduced insulator-metal transition. We report a new fabrication method for thin film samples of the Ni compounds. Using these thin film samples, we have performed femtosecond pump-probe spectroscopy. Photomodulated absorption induced by resonant and nonresonant photoexcitation on charge-transfer band have revealed that excitons decay very fast with the time constant $\tau$ less than 2 picoseconds and charge carriers decay relatively slow with $\tau > 20$ ps. The slower decay of the charge carriers is attributable to the formation of polarons and the resultant decrease of their mobility.

1. Introduction

As the development of optical communication networks progresses, the demand for ultrafast optical switching with terahertz operation is rising. Nonlinear optical materials with large third-order nonlinear susceptibility $\chi^{(3)}$ and a small relaxation time $\tau$ of the photoexcited states are indispensable to realize such operations. Recently it has been reported that one-dimensional (1D) Mott insulators of halogen-bridged nickel-chain compounds exhibit large $\chi^{(3)}$ and small $\tau$. Previous nonlinear optical measurements such as electro-reflectance and third-harmonic-generation spectroscopic studies have revealed that [Ni(chxn)\textsubscript{2}Br]Br\textsubscript{2} shows the largest $\chi^{(3)}$ among 1D semiconductors [1, 2]. Although these studies have clarified the physical background of large $\chi^{(3)}$ of the Ni compounds, there are no measurements of the magnitude of two-photon absorption (TPA) and optical Kerr effect, which are most important properties for all-optical switching operations. In addition, the mechanism of the ultrafast relaxation of photoexcited states in the compounds has not been fully understood yet.

In this paper, we report the results of the Z-scan measurement and femtosecond pump-probe spectroscopy on newly developed thin film samples of Br-bridged Ni compounds [3, 4]. With the thin film samples of Ni compounds we can perform various nonlinear optical measurements and more precise spectroscopy in transmission configurations than in reflection configurations on single crystals.

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2. Experiment

Thin film samples of the Ni compounds were obtained by dispersing fine crystals into optically transparent polymers. To overcome the low solubility of \([\text{Ni(chxn)}_2\text{Br}]\text{Br}_2\) and other previously studied Ni compounds in organic solvents, we introduced a long alkyl chain (C\(_{14}\)H\(_{29}\)) in the ligand molecule of the compounds [5]. We obtained the thin film samples by dispersing nanocrystals of \([\text{Ni}(\text{L})_2\text{Br}]\text{Br}_2\) (L: 1,2-diaminohexadecane) into Poly(methyl methacrylate) [3]. The absorption spectrum of the \([\text{Ni}(\text{L})_2\text{Br}]\text{Br}_2\) film is shown in figure 1 together with the spectrum of a single crystal of \([\text{Ni(chxn)}_2\text{Br}]\text{Br}_2\). The latter was obtained as the sum of the polarized absorption spectra, which were calculated through the Kramers-Kronig transformation from the polarized reflectivity spectra for the electric field of light parallel and perpendicular to the 1D chain. The sharp peak at 1.3 eV in \([\text{Ni(chxn)}_2\text{Br}]\text{Br}_2\) is attributable to the charge-transfer (CT) transition from the Br 4p to Ni 3d upper-Hubbard band. A similar peak is observed at the same energy in the spectrum of the \([\text{Ni}(\text{L})_2\text{Br}]\text{Br}_2\) film, demonstrating that the compound consists of the same Ni-Br chains as \([\text{Ni(chxn)}_2\text{Br}]\text{Br}_2\).

\(\chi^{(3)}(\omega, -\omega, -\omega, \omega)\) of this film sample was evaluated by the Z-scan method and photomodulated absorption dynamics was measured by pump-probe spectroscopy. As a light source, a Ti:sapphire regenerative amplifier with 1 kHz repetition rate was employed. Output from the amplifier with the pulse width of 130 fs was used for the excitation of optical parametric amplifiers.

![Figure 1. Absorption spectra of a \([\text{Ni(chxn)}_2\text{Br}]\text{Br}_2\) single crystal (broken line) and a \([\text{Ni}(\text{L})_2\text{Br}]\text{Br}_2\) thin film (solid line).](image1)

![Figure 2. A typical Z-scan profile of the thin film measured at 0.80 eV in an open aperture condition.](image2)

3. Results and discussions

A typical Z-scan profile of the \([\text{Ni}(\text{L})_2\text{Br}]\text{Br}_2\) film measured at 0.80 eV, which corresponds to the optical communication wavelength 1.55 \(\mu\)m, is presented in figure 2. The decrease of transmittance around \(Z=0\) confirms that nonlinear absorption occurs around the focal point of the incident light (\(Z=0\)). The variation in the transmittance \(\Delta T\) is proportional to the incident power that indicates the observed signals are due to the third-order nonlinear optical response. The one-photon absorption is negligible at 0.8 eV, which indicates that this nonlinear signal is attributable to TPA. From Z-scan profiles, we evaluated \(\text{Re} \chi^{(3)}(\omega, -\omega, -\omega, \omega)\) and \(\text{Im} \chi^{(3)}(\omega, -\omega, -\omega, \omega)\) at 1.55 \(\mu\)m, which are very large, namely \(-1.5\times10^{-9}\) and \(0.56\times10^{-9}\) esu, respectively. This is the first measurement of \(\chi^{(3)}(\omega, -\omega, -\omega, \omega)\) essential for all-optical switching in halogen-bridged Ni compounds.

In the pump-probe measurements, we selected two pump energies (\(\hbar\omega_p\)), 1.55 eV and 1.28 eV, to discriminate the responses of excitons and charge carriers. The result of a previous photoconductivity measurement confirms that photoexcitation mainly products excitons for \(\hbar\omega_p = 1.28\) eV, and charge carriers in addition to excitons for \(\hbar\omega_p = 1.55\) eV [6]. Therefore the difference between the transient absorption spectra and their dynamics in two excitation conditions reflects the difference of the initial photoexcited states. To discuss relaxation dynamics, as shown in figure 3, we decompose the dynamics into four components, namely an ultrafast-decay component (UDC) with the time constant 0.18 ps, a fast-decay component (FDC) with 1.4 ps, an error-function component (EFC) represented...
by \( \text{erf}(3.0\text{ ps} \cdot t^{-1})^{0.5} \), and a step-function component (SFC). EFC expresses the geminate recombination processes of a pair of two particles after random walks on a 1D chain, and therefore, it is attributable to bleaching caused by photogenerated charge carriers. Meanwhile, the spectral shape of FDC is almost similar to the inverted absorption spectrum as shown in figure 4, so that this component can be assigned to bleaching of the CT band due to the generation of excitons. In fact, the ratio of EFC to FDC for \( h\omega_p = 1.55\text{ eV} \) is significantly larger than that for \( h\omega_p = 1.28\text{ eV} \). This bears out our assignments because of efficient photogeneration of charge carriers with the higher-energy excitation. UDC and SFC, which are not emphasized in this paper, are attributable to coherent nonlinear optical processes and thermal broadening of the CT transition peak, respectively.

Now, we focus on dynamics of excitons and charge carriers, in other words dynamics of FDC and EFC. The decay of charge carriers is much slower than excitons, dominating the response around a few tens of picoseconds after photoexcitation. This slower decay of charge carriers represented by the error function indicates that charge-lattice coupling leads to the localization of carriers, which move along 1D chains via hopping processes. On the other hand, the decay time of excitons is as small as 1.4 ps, which is much smaller than the decay times of excitons in conventional semiconductors which are the order of nanoseconds. This indicates that the energy of an exciton should be transferred rapidly to the lattice and/or spin systems. Such an ultrafast decay of excitons is an essential property of 1D Mott insulators.

![Figure 3](image1.png)

**Figure 3.** Time characteristics of changes in absorption probed at 1.37 eV (dots) due to photoexcitation at (a) 1.55 eV and (b) 1.28 eV. Lines are the fitted results of the dynamics and their components.

![Figure 4](image2.png)

**Figure 4.** (a) Transient absorption spectra with the excitation at 1.28 eV. (b) Spectra of FDC and EFC. A solid (broken) line is the spectrum of the (inverted) optical density.

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