Transient photo-induced phenomena in vacancy-controlled Co-Fe cyanides

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Abstract. Time-resolved absorption spectra have been investigated for vacancy-controlled films of Na1.23Co[Fe(CN)6]0.92.9H2O and Na0.46Co[Fe(CN)6]0.713.8H2O, whose electronic configuration is Co III - Fe II and Co II - Fe III, respectively. In both the films, we observed absorption saturation at 2.3 eV, and ascribed it to formation of anti-state. We found that the charge dynamics is qualitatively different between two films.

1. Introduction

The photo-induced phase transition (PIPT) phenomena have been reported for various materials. Ultrafast time-resolved experiment is a powerful tool to study the dynamics of PIPT, such as insulator-to-metal transition in VO2 [1], Mott transition in halogen-bridged Nickel-chain compound [2] and so on. Kamioka et al. [3] applied the spectroscopy to nano-particles of Co II[FeIII(CN)6]0.675H2O and found lifetime elongation of charge-transferred state with increase in excitation power at 10 K. This observation implies formation of photo-induced hidden phase [3].

Prussian Blue-type transition metal cyanides Na xCo[Fe(CN)6]yzH2O, consists of a rock salt-type cyano-bridged metal network, are also possible platform for the systematic investigation of PIPT dynamics [4, 5]. The Co-Fe cyanide takes two electronic configuration, that is, low spin (LS) phase [CoIII(t2g6eg0; S=0) - FeII(t2g6eg0; S=0)] and high spin (HS) phase [CoII(t2g5eg2; S=3/2) - FeIII(t2g5eg0; S=1/2)]. The electronic phases can be controlled by concentration of [Fe(CN)x] vacancy (1-y) [6, 7]. In this paper, we applied a femtosecond time-resolved spectroscopy to the charge-transfer dynamics in vacancy-controlled Co-Fe cyanide films with different electronic configuration.

2. Experimental

Two kind of Co-Fe cyanide film, Na1.23Co[Fe(CN)6]0.92.9H2O and Na0.46Co[Fe(CN)6]0.713.8H2O, were electrochemically synthesized on ITO transparent electrodes. Details of the film synthesis procedure were described in literatures [6, 7]. The former is in LS phase up to 350 K, while the latter is in HS phase at 300 K. Hereafter, we call the films as “LS film” and “HS film”, respectively. The film thickness was 0.60 μm for the LS film and 1.1 μm for the HS film, which were estimated from the experimentally-obtained optical density together with the absorption coefficient. X-ray diffraction pattern of the film can be indexed with the face-cantered cubic cell (Fm3m; Z = 4).

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Time-resolved absorption spectra were obtained with a pump-probe method at room temperature using a regenerative amplified Ti: Sapphire laser, having a pulse width of 100 fs and a repetition rate of 1 kHz. The pump pulse energy was 1.55 eV and reduced to 500 Hz by optical chopper to provide "pump-on" and "pump-off" conditions with respect to each probe pulse. The white probe pulse was focused in the pump spot on the sample. The transmitted probe spectrum was detected by a Si-photodiode array detector attached to an imaging spectrometer and recorded through a high-speed multi-channel A/D converter. The differential absorption spectrum was calculated from the recorded data for 4 thousands of pulses as a function of probe delay time. We can measure the absorption change with this system between 1.2 eV and 2.7 eV up to 650 ps after pulse excitation [3, 8].

3. Results and Discussion
In the LS film (Fig. 1(a)), an absorption band was observed at ~2.3 eV (hatched area) together with absorption bands above 3 eV (dashed lines), which are expressed by the least-square-fitted lines with Gauss functions. The lower-lying band is ascribed to the charge transfer of an electron from FeII site to the CoIII site. We will call the band as charge-transfer (CT) band. The higher-lying band is ascribed to the inter-molecular transition of [FeII(CN)6] [7]. In the HS film (Fig. 1(b)), the lower-lying band (hatched area) is ascribed to the charge transfer of an electron from CoII site to the FeIII site. The higher-lying bands (dashed lines) are ascribed to the inter-molecular transitions [FeIII(CN)6] [6].

The lower panels of Fig. 1 show the differential absorption spectra at a delay time of 600 ps. The excitation photon energy (downward arrows) corresponds to the tail region of the CT band. In both the films, the differential spectra show negative change around the CT band, indicating that the signal is ascribed to the photo-created charge-transfered state, that is, CoII-FeIII state for the LS film and CoIII-FeII state for the HS film. We call the charge-transfered state as “anti-state”. Thin lines in the lower panels show the differential absorption spectra for temperature change from 300 K to 315 K. Here, we emphasize that the spectra are qualitatively different from the thermally differential spectra. This clearly indicates that the photo-induced signal cannot be ascribed to conventional heating effects.
Fig. 2 (a) and (b) show the temporal behavior of the absorption saturation for the LS film and the HS film, respectively. In both the films, rise time of the absorption saturation is below 4 ps, which is the minimum time step. The transient absorption profiles were analyzed with a Gauss function at every delay time. In the LS film, spectral weight gradually decreases with a decay time of 260 ps and full width of half maximum (FWHM) of the band is nearly constant (= 0.64 eV). Creation efficiency of the anti-states is estimated to be 1.5 at 600 ps. In the HS film, however, spectral weight gradually increases with time up to ~400 ps, and then becomes nearly constant. In addition, FWHM increases from 0.35 eV at 10 ps to 0.57 eV at 600 ps. Creation efficiency of the anti-state is estimated to be 12 at 600 ps. These observations clearly indicate that cooperative effect plays a significant role in the HS film, making a sharp contrast with the LS film. To clarify the origin of the cooperative effect, however, a more systematic investigation is indispensable, which is under progress.

4. Conclusion

We have performed time-resolved absorption spectroscopy to investigate the charge-transfer dynamics in vacancy-controlled films of Na$_{1.23}$Co[Fe(CN)$_6$]$_{0.90}$2.9H$_2$O and Na$_{0.46}$Co[Fe(CN)$_6$]$_{0.71}$3.8H$_2$O with different electronic configurations. We observed transient absorption saturation around the CT band, and ascribed it to photo-created anti-state. We found a qualitative difference in the charge dynamics between two films, perhaps reflecting different interaction between the anti-state and the lattice system.

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