Photoinduced dynamics of prussian blue type cyanide

Y. Moritomo1,2, T. Nakagawa1, Y. Fukuyama1, N. Yasuda1, H. Oosawa1, J. E. Kim1, H. Kamioka1,2, K. Kato3, Y. Tanaka3, S. Kimura1, F. Nakada2, S. Ohkoshi4, H. Tanaka1, M. Takata3

1Japan Synchrotron Radiation Research Center/SPring-8, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo, 679-5198, Japan, 2Department of Physics, University of Tsukuba, Tsukuba 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan, 3RIKEN SPring-8 Center, Harima Institute, 1-1-1 Kouto, Soyo-cho, Sayo-gun, Hyogo 679-514, Japan, 4Department of Chemistry, University of Tokyo, Tokyo 113-0033, Japan.
moritomo@sakura.cc.tsukuba.ac.jp

Abstract. Charge and lattice dynamics has been investigated for Na0.79Co[Fe(CN)6]0.902.9H2O film at 300 K by means of the time-resolved x-ray diffraction apparatus coupled with the in situ time-resolved absorption measurement. We observed an uniform lattice expansion whose relaxation time is ~ 40 ns. Based on the close correlation between the charge and lattice dynamics, the lattice expansion is ascribed to the photo-created charge-transferred Co2+ - Fe3+ state.

1. Introduction

The photo-induced phenomena have been extensively investigated both from the fundamental and technical points of view. In an extreme case, the photo-excitation causes a macroscopic structural change, or the so-called photo-induced phase transition (PIPT). Among the photo-sensitive materials, the Prussian blue type Co - Fe compound, whose formula is A1xCo[Fe(CN)6]yzH2O (A= Na, K, Rb, Cs), is attracting renewed interest of material scientists, because they show a photoinduced magnetization [1] as well as a photoinduced structural change [2]. The compound consists of the rock-salt-type (NaCl-type) cyano-bridged metal network, - CN - Co - NC - Fe -. The compound has two electronic phases, that is, low-spin (LS) phase, Fe2+ (t2g6) - Co3+ (t2g6), and high-spin (HS) phase, Fe3+ (t2g5) - Co2+ (t2g5e2g). Lattice constant of the HS phase is 3% larger than that of the LS phase, reflecting the larger ionic radius of the high-spin Co2+. Recently, Kamioka et al.[3,4] have performed a femtosecond time-resolved spectroscopy for the Co – Fe compound, and observed photo-created charge-transfer state whose lifetime is several ns. They further observed lifetime elongation behavior as excitation power density increases, which is a precursor of formation of photoinduced hidden phase.

The time-resolved x-ray diffraction experiment with use of 3rd generation synchrotron radiation (SR) facility is undoubtedly powerful tool to clarify the mechanism of PIPT and to identify the hidden phase. Recently, we have developed a time-resolved x-ray diffraction apparatus coupled with in situ time-resolved optical measurement [5], and successfully adopted the apparatus to digital versatile disc (DVD) media and clarified its crystallization process [6]. Here, we report the charge and lattice dynamics for the Co – Fe compound with this apparatus.

2. Experimental

© 2009 Yamada Science Foundation and IOP Publishing Ltd
2.1. Sample preparation and characterization
Films of Na$_{1.6-\delta}$Co$_{0.902.9}$H$_2$O ($\delta = 0.81$) were electrochemically synthesized on ITO transparent electrodes (sheet resistance was 100 $\Omega$) under potentiostatic condition at -0.5 V versus a standard Ag/AgCl electrode in an aqueous solution containing 0.8 mmol/L K$_3$[Fe(CN)$_6$], 0.5 mmol/L Co(NO$_3$)$_2$ and 5 mol/L Na(NO$_3$) [7,8]. Hole-concentration $\delta$ of the film was controlled by the oxidization of the film at 0.4 - 0.6 V versus a standard Ag/AgCl electrode in 0.5 mol Na(NO$_3$) aqueous solution. X-ray diffraction pattern of the film can be indexed with the face-cantered cubic cell (Fm$\bar{3}$m; $Z=4$). The film thickness was 1600 nm, which was estimated by the experimentally-obtained optical density together with the absorption coefficient [2]. We investigated temperature variation of lattice constant $a$, and found that the film remains in the LS phase up to 350 K.

2.2. Time-resolved x-ray diffraction system
The time-resolved diffraction measurements were carried out in a new experimental hutch (EH2) at SPring-8, BL40XU[5] in a pump-probe configuration. A regenerative amplified Ti:sapphire laser with a pulse width of 130 fs and wavelength at 800 nm was used as a light source. Output timing of the oscillator is synchronized to 84.76 MHz, which is 1/6 of a master oscillator of the RF system for the storage ring acceleration (508.58 MHz). The excitation photon energy was 1.55 eV, the power density was 9 mJ/cm$^2$, and the spot size was 100 $\mu$m x 450 $\mu$m. Delay time between pump laser pulse and the probe x-ray pulse (948.98Hz) was controlled by phase shift of the master oscillator (Timing clock delay system [9]). This method allowed us to change the delay time by a nearly infinite amount with precision of 8.40 ps. The undulator gap at BL40XU can be varied so that the fundamental radiation is altered from 8 to 17 keV. A single bunch x-ray pulse (3 mA and 80 ps) was selected with an X-ray pulse selector (XPS). The x-ray pulse was monochromized by a Si(111) channel-cut monochromator. The probe x-ray wavelength was 1.02924 Å and the spot size was 30 $\mu$m x 320 $\mu$m.

The sample film was placed on a high-precision diffractometer system, which consists of high-precision $\theta$-2$\theta$ goniometer system and 100-nm-resolved XYZ sample positioning stages. Diffraction pattern was recorded with an imaging plate (IP) detector. Typical exposure time was 4 hours. In order to avoid possible sample damage by the photo-excitation and/or x-ray-irradiation, the Z-axis of the sample is continuously moved by several mm during the exposure time and the X-axis is moved prior to each measurement. We further performed the in situ time-resolved absorption measurement at 532nm. This simultaneous measurement excludes possible ambiguities between the two measurements, and enables us to directly compare the charge and lattice dynamics.

3. Results and Discussion
3.1. Photoinduced charge in the x-ray diffraction pattern
We show in Figure 1(a) the time-resolved x-ray diffraction patterns for Na$_{0.79}$Co$_{0.902.9}$H$_2$O film at 300 K without pump and at 20 ns after light excitation. The broad background structure is due to the scattering of the glass substrate. Figure 1(b) and (c) are the magnified patterns around (200) and (400) reflections, respectively. In both patterns, the reflection peaks move toward the low-angle side without showing any extra reflection. The rigid shift of the reflection indicates that an uniform lattice expansion, rather than a local lattice distortion, is induced by photo-excitation. The photoinduced lattice change recovers within 1 ms.

Figure 2 shows delay time ($\Delta t$) dependence of the diffraction patterns around (200) reflection for Na$_{0.79}$Co$_{0.902.9}$H$_2$O film at 300 K. With increase in $\Delta t$, scattering angle 2$\theta$ significantly decreases at $\Delta t = 20$ ns, and then gradually recovers. We have refined magnitude of lattice constant $a$ by a Rietveld analysis with the face-cantered cubic model (Fm$\bar{3}$m; $Z=4$).
3.2. Charge and Lattice dynamics

We summarized in Figure 3 (a) charge and (b) lattice dynamics for Na$_{0.79}$Co[Fe(CN)$_6$]$_{0.90}$2.9H$_2$O film at 300 K. As indicated by a gray curve in Figure 3(a), the relative transmittance change $\Delta T/T$ is well reproduced by two exponential functions, whose decay times are 18 ns and 1000 ns. The fast component can be ascribed to absorption saturation of the charge-transfer band [7,8]. Actually, lifetimes of the photo-created charge-transferred states for Prussian blue compounds are several ns [3,4]. On the other hand, the slow component is due to the conventional heating effect.

The lattice dynamics shows a characteristic behavior: the relative lattice constant $\Delta a/a$ shows a fast relaxation with decay time of ~ 40 ns, then gradually increases above ~ 100 ns. Here, we emphasize that the fast relaxation of $\Delta a/a$ roughly correlates with the fast component of the charge dynamics. Then, the fast lattice expansion is ascribed to the photoinduced charge-transferred Co$^{2+}$ - Fe$^{3+}$ state. The excitation power density of 9 mJ/cm$^2$ at 800 nm corresponds to the absorbed photon density of 0.02 photons/Co. The photo-created Co$^{2+}$ species tends to takes the high-spin state, whose ionic radius (= 0.7045 nm) is much larger than that (= 0.0545 nm) of the low-spin Co$^{3+}$. Then, the charge-transferred Co$^{2+}$ - Fe$^{3+}$ states cause local lattice expansion. The uniform lattice expansion, however, implies that a non-local effect around the Co$^{2+}$ sites plays an essential role in PIPT in the Co – Fe system, because only 2% Co$^{2+}$ species induce the fast and uniform lattice expansion.
4. Conclusion

Charge and lattice dynamics has been investigated for Na$_{0.79}$Co[Fe(CN)$_6$]$_{0.90}$2.9H$_2$O film at 300 K by means of the time-resolved x-ray diffraction system coupled with the \textit{in situ} time-resolved absorption measurement. We observed the correlation between the charge and lattice dynamics in the nano-second region. We believe that our apparatus is an ultimate tool to comprehend the mechanism of PIPT, and systematic investigation in the pico-second region is under progress.

References

[1] Sato O, Iyoda T, Fujishima A and Hashimoto K, 1996 \textit{Science}, 272 704
[2] Hanawa M, Moritomo Y, Kuriki A, Tateishi J, Kato K, Takata M and Sakata M, 2003 \textit{J Phys. Soc. Jpn.}, 72 987
[3] Kamioka H, Moritomo Y, Kosaka W and Ohkoshi S, 2008 \textit{Phys. Rev. B}, 77 180301(R)
[4] Kamioka H, Moritomo Y, Kosaka W and Ohkoshi S, 2008 \textit{J. Phys. Soc. Jpn.}, 77 093710
[5] Kimura S, Moritomo, Y, Takaya Y, Tanaka H, Toriumi K, Kato K, Yasuda N, Fukuyama Y, Kim J E, Murayama H and Takata M, 2007 \textit{Ann. Ist. Phys. Soc.} 879 1238
[6] Fukuyama Y, Yasuda N, Kim J E, Maruyama H, Tanaka Y, Kimura S, Kato K, Kohara S, Moritomo Y, Matusnaga T, Kojima R, Yamada N, Tanaka H, Oshima and Takata M, 2008 \textit{Appl. Phys. Ex.} 1 045001
[7] Nakada F, Kamioka H, Moritomo Y, Kim J E and Takata M, 2008 \textit{Phys. Rev. B}, 77 224436
[8] Igarashi Y, Nakada F and Moritomo Y, preprint.
[9] Fukuyama Y, Yasuda N, Kim J E, Maruyama H, Ohshima T, Tanaka Y, Kimura S, Kamioka H, Moritomo Y, Toriumi K, Tanaka H, Kato K, Ishikawa T and Takata M, 2008 \textit{Rev. Sci. Ist} 79 045107