Ultrafast electronic relaxation dynamics in a valence fluctuation material Sm$_{0.83}$Y$_{0.17}$S

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Abstract. We report ultrafast electronic relaxation dynamics of yttrium-doped samarium monosulfide, Sm$_{0.83}$Y$_{0.17}$S, which is one of valence fluctuating compounds, by pump-probe measurements. We observed a large increase of the Drude weight in the reflectivity spectrum by the photo-excitation and a double exponential decay of the relaxation time to a metastable state. This suggests that the photo-induced effect can be explained as the change of carrier density. The metastable state has a long lifetime (>1 ns) and the carrier density is slightly higher than that before the photo-excitation.

1. Introduction

Samarium mono-sulfide (SmS) is a typical valence fluctuating compound that exhibits the pressure-induced valence transition from divalent with black insulating (BI) phase to trivalent with golden metallic (GM) phase, namely the black-golden (BG) transition at the pressure of about 0.65 GPa [1]. The BG transition also occurs by replacing Sm with yttrium (Y) owing to the smaller ionic radius of Y$^{3+}$ than that of Sm$^{2+}$ [2-4]. The Y substituted material by 17%, Sm$_{0.83}$Y$_{0.17}$S, is located just before the border between black and golden phases [5]. This material exhibits a metallic character but black colour, namely black metallic (BM) phase, which is different from the BI and GM phases appearing in SmS [6,7]. In the BM phase, divalent (Sm$^{2+}$) is stable, but it is located very close to the GM phase with Sm$^{(3-\delta)+}$. Therefore, the valence transition from the BM phase to GM phase might occur due to a photo-excitation from the Sm$^{2+}$ to Sm$^{(3-\delta)+}$ states.

In this study, to investigate the photo-induced valence transition and the electronic structure of the photo-induced phase, we performed an ultrafast pump-probe reflectivity measurement on Sm$_{0.83}$Y$_{0.17}$S. We found that the photo-excited state appears just after the pump-light irradiation and it decays to a new photo-induced phase, namely a metastable state with a double exponential curve. However, the metastable state was concluded not to be the GM phase, so the valence transition did not appear by the photo-excitation.
2. Experimental methods

Single crystals of Sm$_{0.83}$Y$_{0.17}$S having the same NaCl-type crystal structure as SmS were grown by the Bridgman method. To perform the ultrafast pump-probe reflection spectroscopy, a Ti: sapphire regenerative amplifier (1.55 eV, 70 fs, 1 kHz) was used as the pump and probe light sources. The photon energy (wavelength) of the pump beam was fixed as 1.55 eV (800 nm). On the other hand, the photon energy (wavelength) of probe beam was tuned from 0.48 eV (2600 nm) to 2.07 eV (600 nm) by using an optical parametric amplifier. The spot size of the pump beam at the sample position is about 2 mm in diameter.

3. Results and Discussion

Figure 1(a) presents the time-evolution of the reflectivity change ($\Delta R/R$) at several photon energies. At higher energy side, the reflectivity greatly increases immediately after the photo-excitation. The time-evolution of $\Delta R/R$ after the great increase shows a double exponential decay with a constant background with a longer lifetime than 1 ns, but it will be recovered in the repetition time of 1 ms. This suggests that the photo-excited state is relaxed to a metastable state with the long lifetime.

Before the photo-excitation, the reflectivity spectrum increases with decreasing photon energy, suggesting the existence of carriers explained by the Drude model as shown by the red line in Fig. 1(b). Using this spectrum, we can obtain time-dependent reflectivity spectra. The spectra just after photo-excitation and in the metastable state are shown by green squares in Figs. 1(b) and 1(c), respectively.

Figure 1 (a) Time-evolution of reflectivity change ($\Delta R/R$) after the photo-excitation at several probing photon energies. Each curve is shifted in the vertical direction by the step of 0.1 eV. (b) Reflectivity spectrum at 0 ps (just after the photo-excitation) indicated by green line. Red line is the spectrum at -1 ps (before the photo-excitation). Blue line is the same as the red line but the energy is shifted by 0.115 eV. (c) Reflectivity spectrum in the metastable state at 300 ps after the photo-excitation indicated by green line. Red line is the spectrum before photo-excitation (same as the red line in (b)) and blue line is the same spectrum as the red line but the energy is shifted by 0.02 eV.
The spectrum after the photo-excitation (green line) agree with the energy-shifted spectrum (blue line) in Figs. 1(b) and 1(c), respectively.

In the Drude model, the energy shift of the slope as well as the plasma edge \((\hbar \omega_0)\) corresponds to the change of the carrier density, i.e., the increase of the reflectivity intensity \((\Delta R/R)\) after the photo-excitation can be explained by the increase of the Drude weight as well as the increase of carrier density. The increase of the carrier density corresponds to twice as much as the energy shift. As shown in Fig. 1(b), the spectrum after the photo-excitation (green line) is very similar to the spectrum before the photo-excitation \((\hbar \omega_0 \sim 1.7 \text{ eV})\) with the energy shift by 0.115 eV (blue line), i.e., the carrier density increases by about 16 % due to the photo-excitation.

In the metastable state, on the other hand, the obtained spectrum (green line) is consistent with the spectrum with the energy shift by 0.02 eV (blue line) as shown in Fig. 1(c). The increase of the carrier density by the photo-excitation is only about 3 %.

Figure 2(a) shows the excitation-power dependence of \(\Delta R/R\) at 1.55 eV (probe beam). With increasing excitation power, the reflectivity increases. The time-evolution of \(\Delta R/R\) can be expressed by the equation with a double decay process as shown by black lines in Fig. 2(a); \(\Delta R/R = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2) + I_3\). The lifetimes \((\tau_1 = -0.35 \text{ ps} \text{ and } \tau_2 = -4.2 \text{ ps})\) do not change with the excitation-power shown in the inset of Fig. 2(a), but the constant value \(I_3\) only changes. Figures 2(b) and 2(c) show the excitation-power dependences of the peak intensity of \(\Delta R/R\), which is the intensity of the photo-excited state, and the constant term \(I_3\), which is the intensity of the metastable state, respectively. As shown in Fig. 2(b), the peak intensity of \(\Delta R/R\) monotonically increases as the excitation-power increases. This result suggests that the plasma frequency increases with increasing excitation-power, i.e. the number of the photo-excited carriers increases. In the same manner, as shown in Fig. 2(c), \(I_3\) also monotonically increases with increasing excitation-power, suggesting that the photo-excitation only produces photo-carriers but does not cause a phase transition.

Even though the carrier density increases after the photo-excitation, the metastable state is not the same as the GM phase. The BG transition might need other effects such as lattice relaxation.

Figure 2 Excitation-power dependence of the time-evolutions of \(\Delta R/R\) (colour lines; experimental results, black lines; fitting curves) (a), lifetimes \(\tau_1\) and \(\tau_2\) (inset of (a)), the maximum value of \(\Delta R/R\) (b), and the constant value \(I_3\) (the intensity of the metastable state) (c). The photon energy of the probe light was set as 1.55 eV.
4. Conclusion
We performed pump-probe measurements on Sm$_{0.83}$Y$_{0.17}$S to investigate the ultrafast electronic relaxation dynamics of valence fluctuation and valence transition. We observed a huge increase ($\Delta R/R > 0.8$) of the reflectivity just after the photo-excitation and a double exponential relaxation to a metastable state. The reflectivity spectrum of the photo-excited state can be explained by the increase of the Drude weight, suggesting the carrier density increases after the photo-excitation. The metastable state has a long lifetime (>1 ns) and slightly high carrier density. However, the metastable state is not the GM phase but is still in the BM phase even with the maximum excitation-power at 100 mW.

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