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Slow Dynamics of the Photoinduced Phase Transition in Pd(dmit)$_2$ Salts (dmit = 1,3-dithiol-2-thione-4,5-dithiolate)

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Slow dynamics of the initially photoinduced state has been observed by the pump–probe type time-resolved reflection spectroscopy in the charge separated phase of the half-filled strong dimer system, $Et_2Me_2Sb[Pd(dmit)_2]_2$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate). We have succeeded to reproduce the probe photon energy dependence of the time profile qualitatively in the time delay range from 10 ps to 1 ns assuming the dynamical expansion of the domain of the photo-induced dimer-Mott insulating phase in the host charge-separated one.

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1. Introduction

In recent developments in materials science, the search for crystals with highly efficient and ultrafast photoresponse, so-called photoswitching materials, has occupied an important place in both fundamental and applied studies. In this view point, molecular conductors are great candidates for such materials since there are cooperative/competing interactions among lattice, electronic and molecular structures. Therefore, various photoinduced phase transition (PIPT) phenomena have been observed in this class of organic materials [1–3].

Among them, newly developed materials, $Et_2Me_2Sb[Pd(dmit)_2]_2$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate) are unique dimer systems which show charge-separated (CS) phase at low temperatures [4, 5]. These compounds crystallize in a layered structure, in which conducting anion layers made of Pd(dmit)$_2$ (the molecular structure is shown in Fig. 1) and insulating cation layers of Et_2Me_2Sb are alternately stacked [6]. In the anion layer, Pd(dmit)$_2$ molecules are stacked face-to-face with changing directions from layer to layer (along the $\boldsymbol{a}+\boldsymbol{b}$ and $\boldsymbol{a}-\boldsymbol{b}$ axis) to form a solid-crossing structure. The formal charge of Pd(dmit)$_2$ is $-1/2$. However, the system has a half-filling character as a result of very strong dimerization. Reflecting this characteristics of $Et_2Me_2Sb[Pd(dmit)_2]_2$, the high temperature phase is not metallic but the dimer-Mott (DM) insulating one. The strong dimerization in these compounds also plays important role to realize the CS phase due to the HOMO–LUMO interplay [4], thus this phase is a unique phase in these strong dimer systems, Pd(dmit)$_2$ salts.

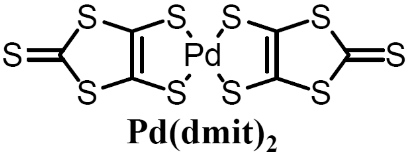

Fig. 1. Molecular structure of Pd(dmit)$_2$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate).

Recently, we have reported the occurrence of the PIPT in this crystal from the host CS phase to DM one [7]. In that case, ultrafast and large reflectivity changes were observed within a time scale of a few ps (< 10 ps). On the other hand, we focus on a slow dynamics observed in a time scale of a few hundred ps in $Et_2Me_2Sb[Pd(dmit)_2]_2$ in this report.

2. Experimental

Single crystals of $Et_2Me_2Sb[Pd(dmit)_2]_2$ were obtained by an oxidation process of $[Et_2Me_2Sb]_2[Pd(dmit)_2]$ in air [6]. We also carried out pump–probe time-resolved reflection spectroscopy measurements. Experimental condition of this study was almost the same as with the previous one [7]. A femtosecond-pulsed laser from a

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Ti:sapphire regenerative amplifier (pulse width 120 fs, photon energy 1.58 eV, repetition rate 1 kHz, Quantronix Integra) was utilized as the light source. The photon energy of probe light was changed using the optical parametric amplifier (OPA, Light conversion TOPAS). The size of the spot of the pump light was adjusted to be around 350 μm diameter and that of the probe light was adjusted to within 50 μm in diameter. The time delay between the pump and probe lights were controlled using the translational stage to create a difference in the optical path length. We used a photodiode type photodetector. In order to accumulate data with a good S/N ratio, we utilized a gated integrator (SR250, Stanford Research Systems). The samples were fixed on a copper-based sample holder and loaded in a liquid He exchange type dynamic flow optical cryostat (Oxford, Optistat) equipped with quartz windows for optical measurements.

3. Results and discussions

We have already reported the dynamics of the PIPT in the CS phase of the $Et_2Me_2Sb[Pd(dmit)_2]_2$ single crystal within 10 ps time scale [7]. The occurrence of the large reflectivity change and its relaxation process were discussed. In the time scale of 10 ps to 1 ns, we found rather complex time profile depending on the probe photon energy with strong excitation intensity and at near the transition temperature ($T_c = 70$ K).

Figure 2a shows obtained time profiles of photoinduced relative change of the reflectivity ($\Delta R/R$). We changed the photon energy of the probe light in an energy range of the intra-dimer excitation in the $Pd(dmit)_2$ dimers. The $\Delta R/R$ showed various kinds of shapes of the time profile depending on the photon energy of the probe light. Most typical shape of the time profile was that of the probe photon energy of 1.31 eV which showed a broad peak at certain time delay. Similar peak in time profile of $\Delta R/R$ has been observed in Co oxide [8] and the origin has been attributed to the propagating motion of the domain boundary of the photoinduced state along the perpendicular direction from the sample surface. Then, we tried to analyse the time profile of $Et_2Me_2Sb[Pd(dmit)_2]_2$ based on similar model.

As described in Ref. [8], we assumed the following variation of the dielectric function (ε) in order to estimate the propagation of the photoinduced domain boundary

$$\varepsilon(z) = \begin{cases} \gamma\varepsilon^{\mathrm{HT}} + (1-\gamma)\varepsilon^{\mathrm{LT}} & (0<z<d^{\mathrm{PI}}),\\ \gamma\exp\left(-\frac{(z-d^{\mathrm{PI}})}{d}\right)\varepsilon^{\mathrm{HT}} + \left[1-\gamma\exp\left(-\frac{(z-d^{\mathrm{PI}})}{d}\right)\varepsilon^{\mathrm{LT}}\right] & (d^{\mathrm{PI}}<z). \end{cases} \tag{1}$$

Here, z is the distance from the sample surface, $\varepsilon^{\mathrm{HT}}$ and $\varepsilon^{\mathrm{LT}}$ are ε at 100 and 50 K which can be attributed to the high temperature (DM) phase and the CS phase, respectively (we assumed that the high temperature phase is a photoinduced state in this analysis), and γ is the yields of the observed PIPT ($0 < \gamma < 1$). The penetration depth of the pump light (1.55 eV), d, was about 50 nm, as estimated by the Kramers–Kronig analysis using measured static optical reflectivity. d^{PI} is the thickness of the photoinduced state, as schematically shown in Fig. 3. For the calculation, we used the multilayer model [9, 10]. Figure 2b shows the calculated $\Delta R/R$ plotted as a function of d^{PI}. If we assumed the d^{PI} increased with constant speed and d^{PI} corresponded to the time delay, the calculated result well reproduced the broad peak structure in the time profile of the observed $\Delta R/R$. The shape of the time profile seems to be reproduced qualitatively by this model especially at around the peak energy of the intra-dimer excitation (about 1.31 eV) in the DM phase, though the absolute value of the $\Delta R/R$ could not be at the photon energy far from the above energy. This qualitative correspondence between the experimental and the calculated results imply that the slow dynamics of the PIPT in this compound were also governed by the propagating motion of the photoinduced domain boundary along the perpendicular direction from the sample surface. Based on this model, we could roughly estimate the velocity of the domain boundary motion using the relation between the d^{PI} and the broad peak position in the time delay. Estimated speed of the domain boundary utilizing the time profile of 1.31 and 1.36 eV was about 600 m/s.

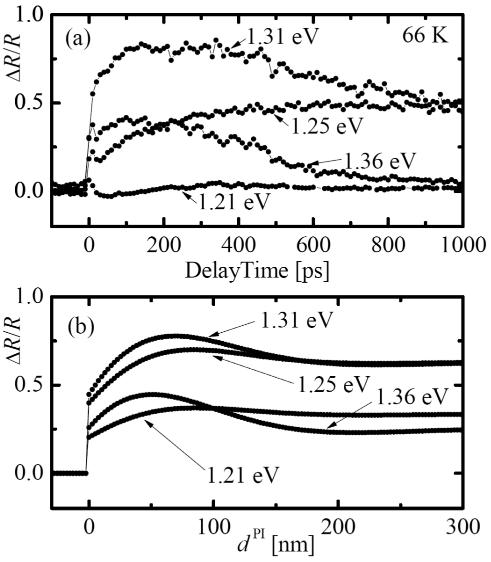

Fig. 2. (a) Time profiles of the photoinduced reflectivity change with various probe photon energy at 66 K. The pump photon energy was 1.58 eV with the strength of 1.42×10^{15} photons/cm^2. (b) The depth (d^{PI}) dependence of the calculated photoinduced reflectivity change with various probe photon energy (see text).

Two mechanisms are proposed as a possible origin for driving the domain boundary motion. The first one is the propagation of the photoinduced coherent phonon similar to $PrCaCoO_3$ [8]. In this case, the velocity of the domain boundary motion should be equal to the sound

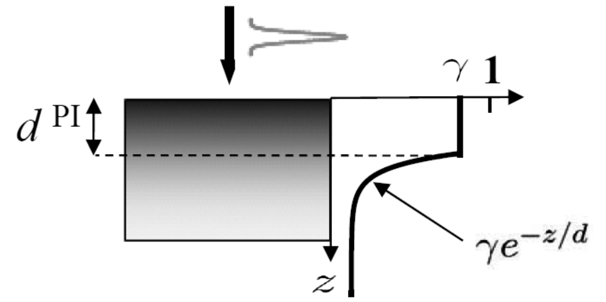

Fig. 3. A schematic view of the spatial variation of the photoinduced state (see text). The z axis represents the direction perpendicular to the sample surface which was irradiated by pump light. γ is the ratio of the photoinduced state and d represents the penetration depth of the pump light.

velocity. However, the estimated value of the velocity for $\mathrm{Pd(dmit)_2}$ salt is rather slower than the sound velocity in the ordinary solid. Another possible mechanism is the thermal activation effect which enhances a diffusive motion of the domain boundary. Of course, the data reported here are not accurate enough to judge which mechanism is dominant in this system. We tentatively conclude that the observed domain boundary motion was due to thermal mechanism, because the time scale for the observed reflectivity change was rather slow compared with the time scale of purely electronic phenomena and the sound velocity in solid.

4. Conclusions

We have observed the slow dynamics of the $\Delta R/R$ due to the domain dynamics of the initially photoinduced state in the CS phase of the $\mathrm{Et_2Me_2Sb[Pd(dmit)_2]_2}$ using the pump–probe type time-resolved spectroscopy. We have succeeded in reproducing the probe photon energy dependence of the time profile of $\Delta R/R$ qualitatively in the time delay range from 10 ps to 1 ns using the model proposed in Ref. [8]. We tentatively assigned the driving force for the domain boundary motion to the thermal diffusive effect.

Acknowledgments

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