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# Photoinduced Phase Transitions over Three Phases in $\mathbf{Ba_{0.9}Sr_{0.1}V_{13}O_{18}}$

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## Abstract

$Ba_{0.9}Sr_{0.1}V_{13}O_{18}$ exhibits two ordered phases caused by the charge/orbital ordering of the $d$ electrons on the V ions. We have succeeded in observing photoinduced phase transitions over three phases in this compound: a transition from the low-temperature phase to the high-temperature phase within 0.3 ps, followed by a transition to the intermediate-temperature phase within 2 ps. The relationship between the symmetry at each of the three phases plays a key role in the dynamics of the photoinduced phase transitions in such a compound.

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Photoinduced phase transitions have been investigated in various strongly correlated electron systems exhibiting intriguing ordered states, for example, Mott insulating states,[1–4] charge-ordered states,[5–7] and orbital-ordered states.[8–10] In many cases, a phase transition from a low-temperature (LT) phase to a high-temperature (HT) phase occurs after a laser pulse is applied, and it is often completed in a time much shorter than 1 ps. This time is not sufficiently long to increase the temperature of the lattice, indicating the electronic origin of the phase transition. Namely, electrons are excited by the application of a laser pulse, and the excited electrons directly suppress the ordered state in the LT phase. Note that photoinduced phase transitions from the HT phase to the LT phase[11,12] or into a hidden phase[13,14] have also been reported.

One of the issues considered in the present study is how the photoinduced phase transition behaves in a system in which more than two thermodynamically stable phases appear with changes in temperatures. In such a case, photoinduced phase transitions over more than two phases are expected. Here, it is known that the characteristics of phase transitions are dominated by the relationship of the symmetry at each phase; the phase transition can be second-order if the symmetry of the LT phase is a subgroup of that of the HT phase, whereas it becomes first-order if there is no such relationship. By utilizing the symmetry and the characteristics of the phase transitions, it may be possible to control the photoinduced phase transitions over more than two phases.

$AV_{13}O_{18}$ (A=Ba, Sr) is a series of compounds that exhibit two different types of ordered states, both of which are dominated by the $d$ electrons on the V ions.[15–17] This series of compounds takes a hexagonal structure and the V ions form a quasi-fcc lattice. The HT phase of these compounds is characterized by V tetramers, in which four V ions in a rhombus shape approach each other and form a cluster, as shown in Fig. 1 (a). It is considered that the ordering of the $t_{2g}$ states in the V $d$ orbitals, as illustrated in the upper left of Fig. 1 (a), is the origin of such V tetramerization. With decreasing temperature, two ordered states can appear in this compound. One is a V trimer phase (defined as the LT phase below), in which three V ions in a regular triangle approach each other and form a trimer instead of a V tetramer, as shown in Fig. 1 (a). It is speculated that this V trimer is also caused by the orbital ordering of the V $t_{2g}$ states, as illustrated in the lower left of Fig. 1 (a). Another phase, defined as the intermediate-temperature (IT) phase, is characterized by the superlattice peak at the $(0, 1/2, 1/2)$ position in the diffraction measurement, indicating a doubling of the unit cell. This is presumably caused by the charge ordering of the V ions having a mixed valence of 2.62+ (2.38 $d$ electrons on average), as shown in the lower right of Fig. 1 (c). For $Ba_{1-x}Sr_xV_{13}O_{18}$ with $x > 0.3$, only the trimer phase appears as the LT phase, whereas the charge-ordered phase appears as the IT phase when $x < 0.3$.[16] Thus, in $Ba_{1-x}Sr_xV_{13}O_{18}$ with $x < 0.3$, three phases, the HT phase, the charge-ordered phase as the IT phase, and the trimer phase as the LT phase, appear with decreasing temperature. Regarding the symmetry of the crystal structure, the space group of both the LT phase and the IT phase ($P\bar{1}$) is a subgroup of that of the HT phase ($R\bar{3}$), but there is no such relationship between the LT phase and the IT phase. Namely, the IT phase is more distant from the LT phase than the HT phase in terms of the symmetry, even though it is located next to the LT phase along the temperature axis.

In the present study, we have performed a pump probe optical spectroscopy measurement of $Ba_{0.9}Sr_{0.1}V_{13}O_{18}$ with $T_{co} = 210$ K (between the HT and IT phases) and $T_{tr} = 80$ K (between the IT and LT phases) to investigate the photoinduced dynamics of this compound having two competing ordered phases. We found that when a pump pulse is applied to the sample in the LT phase, an instantaneous ($t < 0.3$ ps) photoinduced phase transition from the LT phase to the HT phase occurs, which is followed by a phase transition to the IT phase within 2 ps.

The single crystal used in the present study was grown by the floating-zone technique, as described elsewhere.[17] The resistivity and the magnetic susceptibility of the crystal are shown in the inset of Fig. 1 (a). A cleaved surface on the $(32\bar{2})$ plane was used for the optical measurement. Reflectivity measurement in the equilibrium state was performed between 0.08 and 5 eV. Time-resolved pump-probe measurement was performed using the light pulse from a Ti:sapphire regenerative amplified laser (wavelength 795 nm, pulse width 130 fs, repetition rate 1 kHz) as a pump pulse, and the light pulse from the same laser that was broadened in frequency ($\hbar\omega = 0.9-2.5$ eV) by self-phase modulation of the light propagating in water was used as a probe pulse. The time resolution in the present experiment was $\sim 0.2$ ps. The polarization of both the pump pulse and the probe pulse was along the $ab$ plane for all the measurements.

Figures 1 (b) and (c) show the reflectivity spectrum $R(\omega)$ and the optical conductivity spectrum $\sigma(\omega)$ derived from the Kramers-Kronig transformation of $R(\omega)$, respectively, at each phase in the equilibrium state. As discussed previously,[17] there is a peak below 0.5

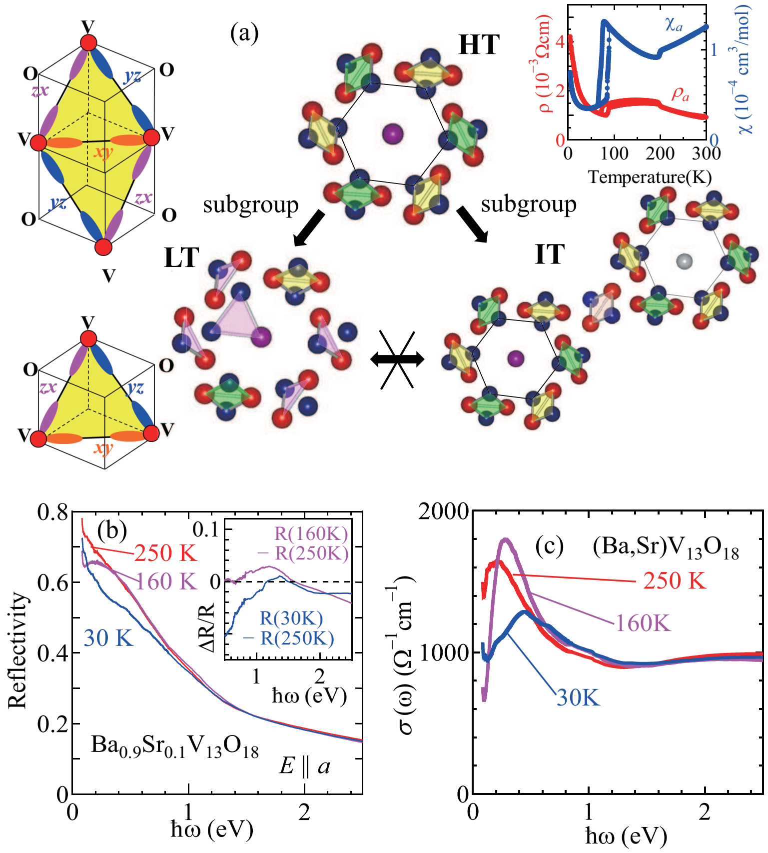

FIG. 1: (Color online) (a) Schematic diagram of the crystal structure for $Ba_{1-x}Sr_xV_{13}O_{18}$ at each of the three phases, the high-temperature (HT), intermediate-temperature (IT), and low-temperature (LT) phases, and the orbital ordering in the V tetramer (upper left) and V trimer (lower left). The upper-right panel shows the resistivity and the magnetic susceptibility for $Ba_{0.9}Sr_{0.1}V_{13}O_{18}$. (b) Reflectivity spectrum at each phase for $Ba_{0.9}Sr_{0.1}V_{13}O_{18}$. (c) Optical conductivity spectrum at each phase for $Ba_{0.9}Sr_{0.1}V_{13}O_{18}$.

eV and a broad structure between 1.5 and 3 eV in the $\sigma(\omega)$ spectrum in this compound, which can be assigned to the in-gap excitation (the excitation of the $d$ electrons between $V^{2+}$ and $V^{3+}$) and the Mott excitation (between $V^{3+}$ and $V^{3+}$), respectively. Characteristic changes in the $\sigma(\omega)$ spectrum with the phase transitions are observed particularly in the in-gap excitation; the peak at $\hbar\omega \sim 0.2$ eV in the HT phase (250 K) shifts to a higher frequency of $\sim 0.3$ eV together with an increase in the peak height in the IT phase (160 K), whereas the peak height is decreased and the peak width is increased in the LT phase (30 K). As a result, the reflectivity from 0.5 to 1.5 eV increases from the HT phase to the IT phase because of the shift of the peak in $\sigma(\omega)$, whereas it decreases to the LT phase because of the suppression of the peak [the inset of Fig. 1 (b)]. Such a non-monotonic change in the reflectivity with the phase transitions makes the analysis of the photoinduced spectral change easier below.

Figure 2 (a) shows the photoinduced change in the reflectivity spectra, $\Delta R/R$, 0.3 ps, 2 ps, and 40 ps after a pump pulse is applied at 50 K in the LT phase. Here, we chose the temperature immediately below the transition temperature ($T_{\rm tr}$) to avoid the problem of supercooling, as discussed in the supplementary information.[18] At $t = 0.3$ ps, a clear dip at 1.2 eV is observed in the photoinduced $\Delta R/R$ spectrum. On the other hand, the $\Delta R/R$ spectrum at 2 ps and 40 ps changes to one in which $\Delta R/R$ almost monotonically decreases with increasing $\hbar\omega$. Figures 2 (b) and (d) show the $t$ dependence of $\Delta R/R$ at various values of $\hbar\omega$ for the probe pulse. At $\hbar\omega = 1.0$ eV or 2.2 eV, the sign in $\Delta R/R$ after the application of a pump pulse is always the same, positive at 1.0 eV and negative at 2.2 eV. However, at $\hbar\omega = 1.2$ eV and 1.7 eV, $\Delta R/R$ becomes negative immediately ($< 0.3$ ps) after a pump pulse is applied, and then it becomes positive and is saturated within 2 ps. This suggests that with the application of a pump pulse to the ground state, it changes to the second phase within 0.3 ps, then it further changes to the third phase within 2 ps.

Figure 2 (c) shows the difference spectrum in reflectivity with $T$ in the equilibrium state, $R(160\text{K}) - R(30\text{K})$ and $R(250\text{K}) - R(30\text{K})$, corresponding to the spectral changes from the LT phase to the IT phase and that from the LT phase to the HT phase, respectively. As can be seen, the photoinduced change in reflectivity at 0.3 ps is similar to the spectral change from the LT to the HT phase, and those at 2 ps and 40 ps are similar to that from the LT phase to the IT phase. This suggests that when a pump pulse is applied to the sample in the LT phase, the state of the sample immediately ($t < 0.3$ ps) changes to the HT phase, and then it is relaxed to the IT phase within 2 ps. The photoinduced $\Delta R/R$ at 0.3 ps at 50 K [Fig. 2 (a)] and the difference spectrum in reflectivity $R(250\text{K}) - R(30\text{K})$ [Fig. 2 (c)] are different in their signs above 2 eV. This is probably due to the fact that the thermal expansion along the plane does not occur within several tens of picoseconds and the absence of such thermal expansion affects the Mott-excitation peak between 1.5 and 3 eV.

We performed the same experiment at 100 K in the IT phase, and the result is shown in Fig. 3 (a). As can be seen, the photoinduced $\Delta R/R$ spectra at $t = 0.3$ ps, 2 ps, and 40 ps are similar, and all resemble the difference spectrum of the reflectivity with $T$, $R(250\text{K}) - R(90\text{K})$ (from the IT phase to the HT phase), shown by the dashed line. Figure

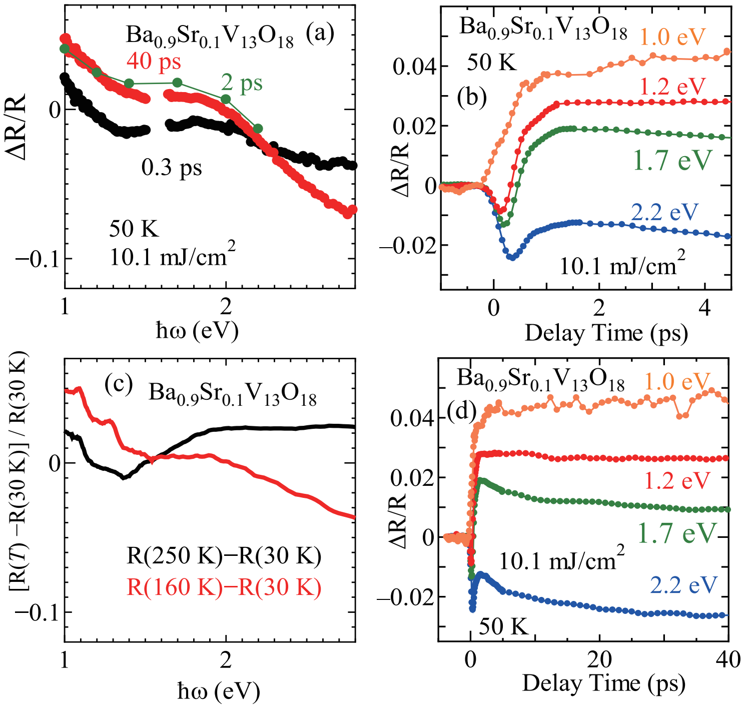

FIG. 2: (Color online) (a) Photoinduced change in the reflectivity spectra 0.3 ps, 2 ps, and 40 ps after a pump pulse is applied to $Ba_{0.9}Sr_{0.1}V_{13}O_{18}$ at 50 K (in the LT phase) (b) Photoinduced change in reflectivity as a function of the delay time up to 4 ps at various values of $\hbar\omega$ for a probe pulse at 50 K. (c) Difference spectra in reflectivity with temperature for $Ba_{0.9}Sr_{0.1}V_{13}O_{18}$. (d) Photoinduced change in reflectivity up to 40 ps.

3 (b) shows the $t$ dependence of $\Delta R/R$. A change in sign of $\Delta R/R$ with $t$, as observed for the photoinduced $\Delta R/R$ in the LT phase, does not exist for the photoinduced $\Delta R/R$ in the IT phase. These experimental results indicate that when a laser pulse is applied to the sample in the IT phase, it immediately ($< 0.3$ ps) changes to the HT phase and then remains in this phase [Fig. 3 (c)]. Note that there are structures in the $t$ dependence of $\Delta R/R$ for $0 - 1$ ps, which also manifests itself in the slight difference between the $\Delta R/R$ spectrum at 0.3 ps and that at 2 ps shown in Fig. 3 (a). This suggests a possible change from the electronically induced HT phase to the thermodynamically stable HT phase, as discussed later for the photoinduced dynamics in the LT phase.

To understand how the LT phase is changed to other phases after a pump pulse is applied, we studied the dependence of the photoinduced $\Delta R/R$ on the intensity (power density) of a pump pulse, $I_{\text{pump}}$, at 50 K. Figure 4 (a) shows the $t$ dependence of the photoinduced $\Delta R/R$

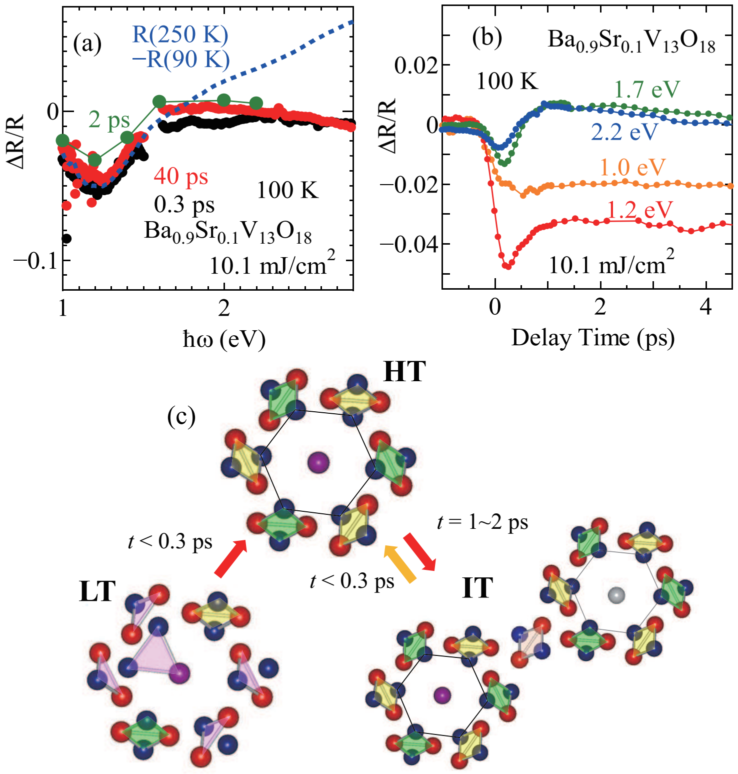

FIG. 3: (Color online) (a) Photoinduced change in the reflectivity spectra 0.3 ps, 2 ps, and 40 ps after a pump pulse is applied to $Ba_{0.9}Sr_{0.1}V_{13}O_{18}$ at 100 K (in the IT phase) for. (b) Photoinduced change in reflectivity as a function of the delay time up to 4 ps at various values of $\hbar\omega$ for the probe laser at 100 K. (c) Schematic of the process of the photoinduced phase transitions in $Ba_{1-x}Sr_xV_{13}O_{18}$.

at $\hbar\omega = 1.2$ eV at various values of $I_{\mathrm{pump}}$. The data were fitted by the following function,

$$\frac{\Delta R(t)}{R} = \theta(t)\left\{(A-B)\exp\left(-\frac{t}{\tau}\right)+B\right\}, \tag{1}$$

where $\theta(t)$ is the Heaviside step function, which is convoluted by the response function of the measurement system, $f(t) = \gamma/\pi(t^2+\gamma^2)$ with $\gamma = 0.2$ ps. This functional form of Eq. (1) [schematically shown in the inset of Fig. 4 (b)] means that $\Delta R/R$ becomes $A$ immediately (much faster than the time resolution of the system $\gamma = 0.2$ ps) after the pump pulse is applied and then is relaxed to $B$ with the time constant of $\tau$. The fitting results are shown by the solid lines in Fig. 4 (a), where $\tau \sim 0.14$ ps barely depends on $I_{\mathrm{pump}}$. The dependence of $A$ and $B$ on $I_{\mathrm{pump}}$ is shown in Fig. 4 (b). The absolute value of $A$, corresponding to the immediate response, increases in a superlinear manner with $I_{\mathrm{pump}}$, whereas the $B$ value,

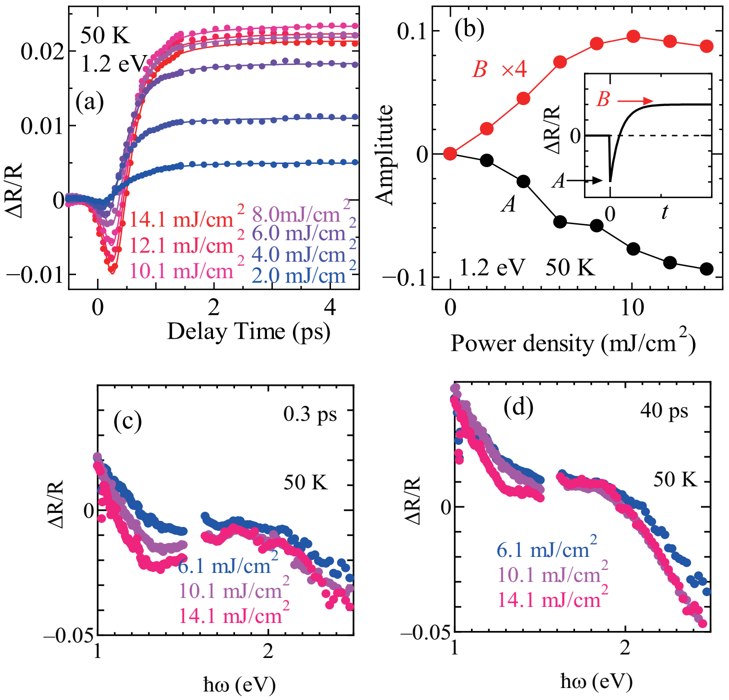

FIG. 4: (Color online) (a) Photoinduced change in reflectivity as a function of the delay time at $\hbar\omega = 1.2$ eV at 50 K for various intensities of a pump pulse. The circles are the experimental data and the solid lines are the fitting curves (see text.) (b) Dependence of $A$ (immediate response) $B$ (delayed response) on the pump pulse intensity. The inset shows a schematic functional form for the fitting (without the convolution). (c)(d) Photoinduced change in the reflectivity spectra for various intensities of a pump pulse at (c) 0.3 ps and (d) 40 ps.

corresponding to the delayed response, increases with $I_{\rm pump}$ but is saturated at $\sim 10\,{\rm mJ/cm}^2$.

Figures 4 (c) and (d) show the photoinduced $\Delta R/R$ spectra at 0.3 ps and 40 ps, respectively, for various values of $I_{\rm pump}$. At 40 ps, the $\Delta R/R$ spectrum hardly changes with $I_{\rm pump}$ and resembles the difference spectrum with $T$, $R$(160K) − $R$(30K), shown in Fig. 2(c).[19] However, at 0.3 ps, the dip at $\hbar\omega \sim 1.2$ eV in the $\Delta R/R$ spectrum, which is a characteristic feature of the difference spectrum between the LT and HT phases [Fig. 2 (c)], deepens with increasing $I_{\rm pump}$.

The result of the fitting by Eq. (1) shown in Figs. 4 (a)(b) clearly indicates that there are two components in the time dependence of $\Delta R/R$ after the application of a pump pulse to the LT phase. The comparison between the photoinduced $\Delta R/R$ spectra [Fig. 2 (a) and Figs. 4 (c)(d)] and the difference spectra in reflectivity with $T$ shown in Fig. 2 (c) indicates that the instantaneous response ($A$) corresponds to the change from the LT phase to the HT phase, whereas the delayed response ($B$) corresponds to the change to the IT phase. It is unlikely that these two processes are both the thermally induced processes occurring in different portions of the sample independently, because (1) there is no reason that the change from the LT phase to the IT phase occurs more slowly than the change from the LT phase to the HT phase, and (2) both $A$ and $B$ increase with increasing $I_{\rm pump}$ experimentally, while if two processes occur in different portions of the sample, the increase in one component will result in the decrease in the other component. Thus, it is most likely that, when a laser pulse is applied to the LT phase, the system immediately changes to the HT phase [corresponding to $A$ in Eq. (1)] and then it relaxes to the IT phase (corresponding to $B$); namely the photoinduced phase transitions over three different phases occur in this compound, as schematically shown in Fig. 3 (c).

As discussed in the introduction, the LT phase is characterized by the V trimer with an orbital ordering of the $t_{2g}$ states, and the symmetry of the LT phase is a subgroup of that of the HT phase. Thus, when a laser pulse causes the excitation of $d$ electrons, it can induce an instantaneous ($t \ll 1$ ps) melting of the orbital ordering (probably without changing the lattice distortion of the V trimers) and can induce a change from the LT phase to the HT phase. Such a scenario of the electronically induced phase transition with photoirradiation is consistent with the superliner behavior in $A$ against the intensity of a pump pulse $I_{\rm pump}$ shown in Fig. 4 (b).[3]

On the other hand, the IT phase has a completely different symmetry from that of the LT phase. Thus, the only way for the system to transfer from the LT phase to the IT phase is to increase the temperature of the lattice such that the IT phase becomes (quasi-)thermodynamically stable. This can be realized by the relaxation of the photoexcited electrons into phononic excitations within $1 - 2$ ps. Such a thermally induced phase transition is consistent with the linear behavior in $B$ for $I_{\rm pump} < 10$ mJ/cm$^2$ and the saturation behavior for $I_{\rm pump} > 10$ mJ/cm$^2$ shown in Fig. 4 (b), since the increase in the temperature of the lattice is simply proportional to the intensity of the pump pulse. It should be pointed out that once the temperature of the lattice is increased, the only way to decrease it is the thermal conduction in the sample, and it takes longer than 1000 ps.[18] This is consistent with the almost time-independent behavior of $\Delta R/R$ from 2 to 40 ps shown in Fig. 2 (d). This also supports the idea of the electronically induced phase transition from the LT phase to the HT phase, since if it is thermally induced, a phase transition from the HT phase to the IT phase does not occur within 2 ps.

In summary, we performed a pump-probe optical spectroscopy measurement on $Ba_{0.9}Sr_{0.1}V_{13}O_{18}$, which exhibits three phases (the LT, IT, and HT phases) at different temperatures. We succeeded in observing the photoinduced phase transitions over three phases, namely, a transition from the LT phase to the HT phase within 0.3 ps followed by a transition to the IT phase within 2 ps when a laser pulse is applied to the LT phase. When a laser pulse is applied to the IT phase, a phase transition to the HT phase occurs within 0.3 ps. The relationship of the symmetry at each phase causes the differences in the time scale for the photoinduced phase transitions in the different phases, meaning that the symmetry plays a key role in the photoinduced phase transitions over the three phases.

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[19] A dip at 1.3 eV in the photoinduced $\Delta R/R$ at 50 K at 40 ps [Fig. 4 (d)] becomes significant with the power density of 14.1 mJ/cm$^2$, and this is probably caused by the fact that a portion of the sample thermally changes to the HT phase with such a high intensity.