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Abstract

The ultrafast carrier dynamics of the multiferroic BiFeO₃ film in a broad temperature range is investigated using optical pump-probe spectroscopy. The photoexcited electrons release their energy with optical phonons emission through electron-phonon coupling in about 1 ps. The following intermediate process is identified as dynamical spin-lattice coupling in several picoseconds. Furthermore, the peak values of the optical reflectivity and the time constants of carrier relaxation channels show significant changes while the temperature varies from 137.5 K to around 195 K, this aligns with the previously reported hidden phase transition. Our study demonstrates that ultrafast spectroscopy is a sensitive method to look into the dynamical interactions among the on-site high-energy electrons accumulated in the p conduction band of Bi, coherent optical phonon, as well as the spin degree of freedom. These features play crucial roles in the characterization of phase transitions.

Keywords

photoexcited, bifeo₃, carrier, film, hidden, phase, transition, dependent, dynamics, temperature, multiferroic

Disciplines

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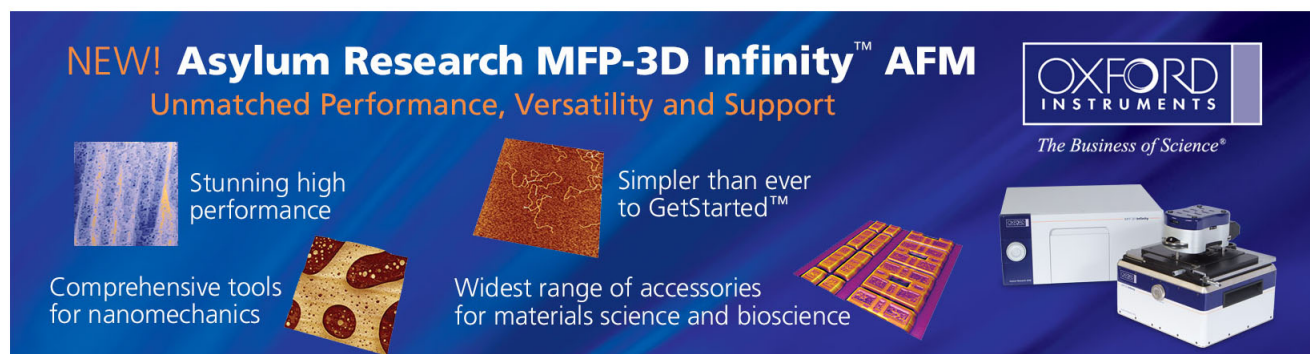
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Temperature dependent photoexcited carrier dynamics in multiferroic BiFeO₃ film: A hidden phase transition

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The ultrafast carrier dynamics of the multiferroic BiFeO₃ film in a broad temperature range is investigated using optical pump-probe spectroscopy. The photoexcited electrons release their energy with optical phonons emission through electron-phonon coupling in about 1 ps. The following intermediate process is identified as dynamical spin-lattice coupling in several picoseconds. Furthermore, the peak values of the optical reflectivity and the time constants of carrier relaxation channels show significant changes while the temperature varies from 137.5 K to around 195 K, this aligns with the previously reported hidden phase transition. Our study demonstrates that ultrafast spectroscopy is a sensitive method to look into the dynamical interactions among the on-site high-energy electrons accumulated in the p conduction band of Bi, coherent optical phonon, as well as the spin degree of freedom. These features play crucial roles in the characterization of phase transitions. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4871689>]

Bismuth ferrite, BiFeO₃ (BFO), has become a canonical material in multiferroic magneto-electric research,^{1–3} not only for its simultaneous ferroelectricity and antiferromagnetism at room temperature (ferroelectric $T_C \sim 1100$ K, antiferromagnetic ordering temperatures $T_N \sim 640$ K) and the large ferroelectric polarization,^{4–7} but also for the intrinsic magnetic-electric coupling at room temperature.⁸ Therefore, the detailed exploration of BiFeO₃'s phase diagram has never stopped.⁶ Recently, a plausible electromagnon was found below room temperature through low energy Raman scattering.⁹ Hitherto, however, the phase transitions or reported anomalies are still controversial issues. The anomalies near 140 K and 201 K had been first observed by Cazayous *et al.* and interpreted as *spin reorientation transitions*.¹⁰ Although, an Almeida-Thouless line terminating at 140 K was attributed to *spin-glass behavior*.¹¹ Sosnowska and Przeniosł carefully measured the neutron diffraction but failed to detect any magnetic structural anomaly below room temperature.¹² Raman,¹³ and THz spectroscopy measurements suggested a *magnetic phase transition* which would cause the similar behavior.¹⁴ Recently, a surface layer phase transition caused by bismuth deficiency near 140 K in BiFeO₃ was proposed, it showed a sharp change in lattice parameter and charge density along surface plane. Meanwhile, the 201 K anomaly appears to signal the onset of spin-glassy behavior.¹⁵

In addition to the static spectra targeting at ground state, ultrafast pump-probe spectroscopy aimed for exciting-state properties was used to unravel the underlying spin-lattice-charge coupling and the magnetic phase transition.¹⁶ In recent years, ultrafast dynamical phenomena have inspired

valuable insights and motivated speed requisite for most electronic devices. The completion of static- and dynamical-optical characterization provides detailed information regarding to the coupling between electronic and magnetic properties in multiferroic materials. Recently, the ultrafast depolarization of ferroelectric order in BFO produces the ultrafast THz radiation.¹⁷ The rapid photo-induced mechanical stress results in the excitation of coherent acoustic phonons and magnons.^{18,19} The dynamics of photo-induced strain was directly and quantitatively measured in a synchrotron-based ultrafast X-ray diffraction.²⁰ One of the most straightforward implementations of ultrafast spectroscopy is the hot electron transient relaxation following the photo-excitation.²¹ In general, as the temperature is lower than the one of a succession of phase transitions, besides the conventional electron-phonon relaxation, additional scattering channels will modify the charge transport and relaxation dynamics.^{22,30}

For better design flexibility, the larger ferroelectric polarization, more steerable magnetism, BFO films have caught more attention.^{5,25,26} In our previous work, we have observed the electron-phonon interaction of BiFeO₃ thin film at room temperature.²⁷ In this Letter, we are interested in the phase transition by characterizing the coupled magnetic and ferroelectric orders in epitaxially grown BiFeO₃ thin film on SrTiO₃ (STO) substrate, through the ultrafast optical pump-probe spectroscopy. The temperature dependent transient differential reflectivity ($\Delta R(t)/R$) allows us to disentangle the different carrier relaxation dynamics in separated phases of BiFeO₃. We find that the electron-phonon and spin-lattice interactions are keys to the carrier relaxation process near the low-temperature anomalies, and the change in the coupling time indicates a lattice-mediated magnetic-electric coupling. The surface magnetic phase transition in BiFeO₃ film is observed through changes in spin-lattice coupling time constant by ultrafast pump-probe spectroscopy.

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Our findings have clarified the competing interactions among electricity, magnetism, and the crystal lattice in BiFeO₃.

The BFO thin film investigated here was grown on (001)-STO substrate using pulsed laser deposition (PLD) with a 355 nm Nd: YAG laser source at a repetition rate of 10 Hz. The deposition was carried out at 600 °C with a dynamic oxygen pressure of 20 mTorr. The film thickness is about 150 nm. Figure 1 shows the X-ray diffraction pattern of the polycrystalline BFO films deposited on (001)-STO. The film is crystallized with rhombohedral-like phase and presents a (012)_h single crystal line orientation according to Ref. 28, rather than previously regarded tetragonal structure.^{27,29} However, comparing with bulk BiFeO₃ with a rhombohedral structure, a slight shifting of (012)_h diffraction peaks to lower 2θ angles was observed, which indicates a trend of distortion toward to tetragonal structure.

The transient reflectivity experiments are carried out with a dual-color pump-probe technique. The light source is a commercial mode-locked Ti: sapphire laser (Spectra-Physics, Spitfire Pro.) operated at a repetition rate of 1 kHz, the pulse width of 120 fs, and the center wavelength of 800 nm. The pump beam with photo energy of 3.1 eV is obtained from a frequency-doubled fundamental beam (800 nm) in a 1-mm β-BaB₂O₄ crystal. The average pump fluence is about 6 mJ/cm² which is 30 times larger than that of the probe. The pump beam which has a center wavelength at 400 nm is normally incident on the sample surface, and the probe beam has an incident angle of about 6° from the normal. The sample was mounted in a closed-cycle liquid-He cryostat in vacuum chamber with four optically accessible windows. The temperature range encompasses the low temperature phase transitions of BFO film but was set right beyond the structure phase transition temperature of SrTiO₃ (103 K).³⁰

Figure 2(a) shows the typical transient reflectivity $\Delta R(t)/R$ at temperatures of 294 K and 160 K, respectively. Electronic photo-excitations by the pump pulses result in a swift rise of $\Delta R(t)/R$ at zero time delay. The pump pulse with the energy of 3.1 eV is larger than the band edge transition ($E_g \sim 2.48$ eV) of BFO film.²⁷ The pump energy corresponds to a minority dipole-allowed oxygen-iron charge transfer excitation and a strongly hybridized majority channel of O 2p + Fe 3d → Bi 6p

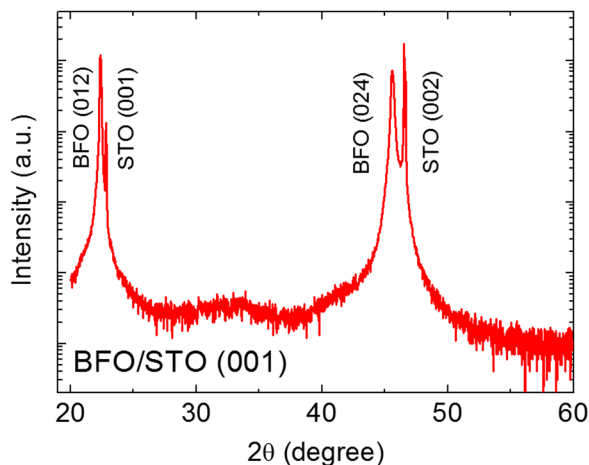


FIG. 1. The x-ray diffraction pattern of the BFO films on (001)-STO substrate.

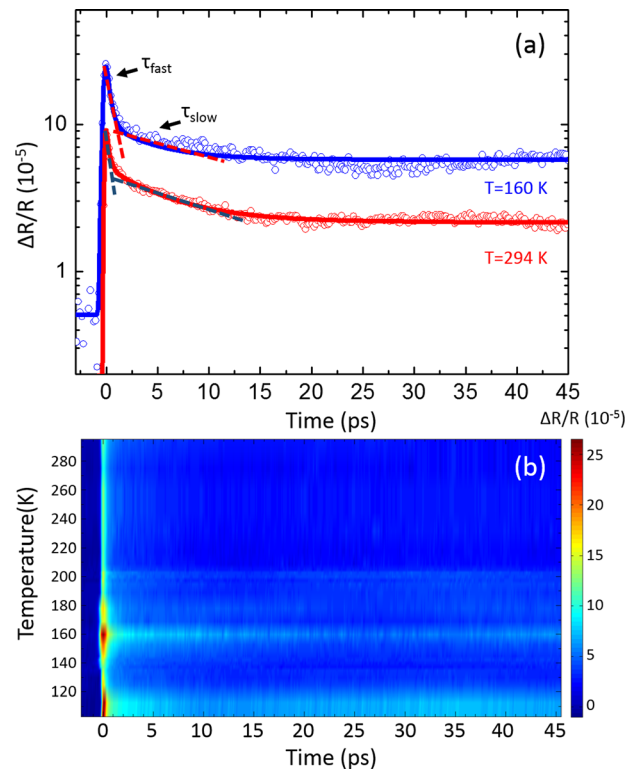


FIG. 2. (a) Logarithmic plot of optical reflectivity change as a function of time delay at two temperatures, 294 K and 160 K, at photoexcited energy of 3.1 eV and probed at 1.55 eV in a BFO film on STO substrate; (b) The optical reflectivity changes as a function of temperature at various time delay.

state excitation.^{31–33} The peak amplitude at zero time delay linearly depends on the number of the photoexcited electrons, as evidenced by the experiment performed at different pump fluence.²⁷ As shown, the $\Delta R(t)/R$ marked by two dashed lines in Fig. 2(a) following the initial photo-excitation. The carrier dynamics show three typical relaxations:^{23–25} (1) the photo-excited electrons rapidly thermalize amongst themselves (electron-electron scattering process, $\tau_{e-e} \sim 100$ fs) and subsequently relax to the minimum of conduction band via electron-phonon coupling. This *fast* component (<1 ps) corresponds to the electron-phonon thermalization; (2) the subsequent *slow* component corresponds to the energy exchange between the lattice and spin system, a dynamical spin-lattice coupling process as explained in more detail below; and (3) the quasi-constant component (\sim ns) has been assigned to a combination of radiative recombination and the heat diffusion out of the illuminated area of the sample,²¹ and this very slow relaxation is beyond the limit of our translation stage. The carrier dynamics are well fitted by a convolution of the Gaussian function $G(t)$ (laser pulse) with a bi-exponential decay function, $\Delta R(t)/R = (A_1 \exp(-\frac{t}{\tau_{fast}}) + A_2 \exp(-\frac{t}{\tau_{slow}}) + A_3) \otimes G(t)$, where A_1 (A_2) and τ_{fast} (τ_{slow}) are the amplitudes and time constants of the fast and slow components, respectively. Fig. 2(b) shows the two dimensional pump-probe spectroscopy with the abscissas for the time and the ordinate for the temperature, a distinct area between the two transition temperatures (137.5–200 K) could be distinguished by the color map. A “slowing down” feature is expected in this temperature range and a seeming step-like change is expected in the longest time constant. This feature is due to the increasing of the peak value and the “slowing down” feature for the former two processes.

It should be mentioned that the slight deviation from the fitting of the long lifetime recombination and the highlight in tens of picoseconds in Fig. 2(b) is due to the coherent acoustic phonon, which was seen to be enhanced efficiently by La and Nb codoped, as previously reported.¹⁸

Further analysis is provided in Figure 3, where the peak value of ΔR ($t=0$ ps) and the time constants, τ_{fast} and τ_{slow} , extracted from the carrier relaxation process as functions of the sample temperature was shown, respectively. Figure 3(a) shows an abnormal (slowing down) temperature dependence of ΔR ($t=0$ ps) at zero time delay, and it is seen that the anomalies occur with beginning at $T_1 \sim 137.5$ K and ending at $T_2 \sim 195$ K. A maximum photo-transition probability appears at around 160 K. The arising of the R_{peak} at around 100 K could be attributed to the structural phase transition of the SrTiO₃ substrate.³⁰ Apart from this instantaneous amplitude, the onset of the two anomalies is further observed in the extracted time constants, as shown in Fig. 3(c). It can be found that magnitude of τ_{slow} slows down significantly, from ~ 3 ps to ~ 6 ps, as the magnetic phase of BiFeO₃ enters into the critical magnetic phase transition temperature at $T_2 \sim 195$ K. The τ_{slow} remains nearly constant value of ~ 6 ps down to the other anomaly occurring at $T_1 \sim 137.5$ K. Our experimental result is evident that the “slow” process can be interpreted as arising from the interaction between the lattice and the spin degree of freedom.

To understand the spin-lattice interaction in the magnetic phase transition of the multiferroic system, we first consider the effects of lattice thermal expansion on the optical band gap, which is strongly related to the reflectivity at probe wavelength. The lattice thermal expansion and

electron-phonon interaction are widely recognized as the reason for the shrinkage in the optical band gap ($\sim 1.3\%$) with the temperature decreasing from 300 to 100 K.³⁴ The longitudinal and transversal optical phonons are the main factors to modify the interatomic distance along and perpendicular to the direction of their propagation with the temperature, respectively. In our case, when the surface magnetic phase transition occurred, an in-plane stress is generated by the magnetic-elastic coupling.¹³ The stress disturbs the lattice constant of the BFO film, which correspondingly moves the conduction band and the valence band downward and upward, respectively. The modification of energy band structure is sensitively probed by the transient reflectivity changes. Similar observations have been reported in multiferroic manganite HoMnO₃, the emergence of long- and short-range magnetic order has been revealed in association with an abnormal blueshift of Mn³⁺ 3d level and the temperature dependent $\Delta R(t)/R$ around the Néel temperature.^{35,36}

By employing low-energy Raman scattering spectroscopy, Cazayous *et al.* reported the anomalies in frequency and intensity of Raman modes as a function of temperature.^{9,10} The anomaly at 140 K is assigned to the spin reorientation transition but with a little coupling to the order parameter in BFO single crystal, and the anomaly at 200 K shows a strong elastic coupling. The temperature dependence of anomalies in Raman mode is in accordance well with our observation: temperature dependence of time constants anomalies. The spin reorientation phase transition in RFeO₃ (R =rare earth ion) is denoted as the rotation of Fe³⁺ magnetic moment from c -axis to a -axis with decreasing temperature. For the case of BFO crystal, the Fe³⁺ magnetic moments are confined in the (121) cycloidal plane in the pseudocubic representation at room temperature. With temperature down to 140 K, a small spin reorientation out of this plane is expected.⁹ Our temperature dependence of time constants anomalies is observed to occur at 137.5 and 194 K in BFO thin film, which shows a little lower than those (140 K and 200 K, respectively) in BFO single crystal observed with Raman spectroscopy. The lower magnetic phase transition temperature observed in BFO thin film might come from thermal fluctuations induced by the laser.³⁴ Here, we mention “surface magnetic phase transition” rather than “spin reorientation transition” in BFO thin film in our case. We would like to mention that the temperature dependence of spin reorientation is not observed with neutron scattering in our BFO film, which indicates that ultrafast spectroscopy is a sensitive way to detect magnetic phase transition such as spin reorientation by monitoring the dynamical spin-lattice coupling.

In contrast to the result that the electron-phonon coupling does not change significantly across the antiferromagnetic transition ($T_N = 623\text{--}643$ K) in BiFeO₃ single crystal,²¹ We find a different and interesting feature of the carrier relaxation in the film sample. The time constant of electron-phonon interaction, τ_{fast} , has a similar temperature dependence with the *slow* component, as shown in Fig. 3(b). In other words, the electron-phonon coupling shows slowing down feature in the magnetic phase transition process. As formulated in first principle calculations,^{37,38} the coupling between the magnetic and mechanical subsystems indicates

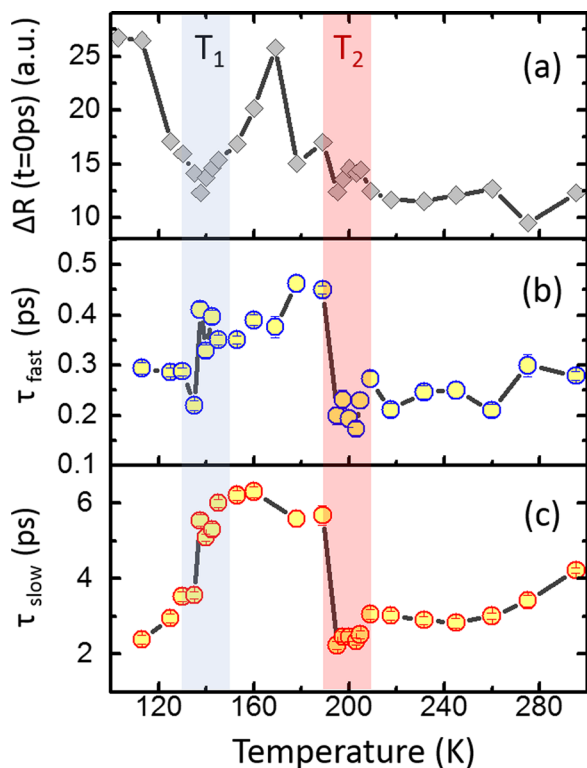


FIG. 3. (a) The amplitude of optical reflectivity at zero delay time $\Delta R(t=0$ ps) as a function of temperature. (b) and (c) The temperature-dependent fast and slow time constants, τ_{fast} and τ_{slow} , respectively.

that the magnetic order has a significant influence on the mechanical systems and modulates the high-energy electrons by releasing their energy through the emission of longitudinal-optical phonons. Up to now, the observed crucial slowing down behavior of the time constants has been demonstrated to the real phase transitions at 195 K and 137.5 K, respectively.

The slow component of the relaxation time is supposed to be the dynamical spin-lattice coupling process. Here, we employ the “three-temperature-model” (TTM) to analysis the pump-probe spectroscopy in magnetic materials.^{23–25} After the initial pump process, the electron temperature raises in more than a thousand Kelvin, which render the two system (electron and lattice) dropped into a nonequilibrium state. The two systems turn into equilibrium state through electron-lattice coupling in 1 ps which is known to be the electron-lattice coupling time (τ_{fast}). Similarly, the lattice and the spin system evolve into equilibrium in several picoseconds which is the dynamical spin-lattice coupling process. After the magnetic phase transition occurs, the magnetic state alters then the atomic lattice positions will be altered for the intrinsic spin-lattice coupling. The temperature dependence of the electron-lattice coupling time clearly shows the transition. From the TTM, the dynamical spin-lattice coupling time is related to the lattice specific heat C_l , spin specific heat C_s , and spin-lattice coupling constant G_{sl} as $\tau_{s-l} \approx \frac{C_s C_l}{G_{sl}(C_s + C_l)}$.^{23–25} The temperature dependent specific heat measurement of BFO across the Néel temperature indicates that $C_s \ll C_l$ in our case.^{39,40} The formula could be simplified to $\tau_{s-l} \approx \frac{C_s}{G_{sl}}$. Thus, the slowing down of the dynamical spin-lattice coupling process represents the change of the spin state of BFO in the magnetic phase transition temperature range independently.

As previous work in Mott-Hubbard insulator LaMnO_3 , the energy of the d-d transitions depends on the spin alignment of the neighboring Mn^{3+} ions. The transitions with spin parallel alignment have larger probability than that with antiparallel alignment.⁴¹ The photo-induced magnon-assisted hopping conductivity leads to a transient reduction of the magnetic order in TbMnO_3 .⁴² Therefore, special care should be taken because the probe beam could be absorbed by additional electronic transitions in BFO. It has been known that the relevant transitions at 1.5 eV are the on-site d-d transition of Fe^{3+} ions. The transitions should be forbidden due to the total spin of change from $S = 5/2$ to $S = 3/2$. However, because the parity selection rule is relaxed through the spin-orbit coupling and the octahedral distortion caused photo-excitations, the transition can occur in BFO.⁴³ This needs further studies to understand the optical transitions under different magnetic structure controlled by epitaxial strain or external magnetic fields.

In conclusion, a hidden magnetic phase transition in BiFeO_3 has been observed independently by ultrafast optical pump-probe spectroscopy. We proffer the electron-phonon and dynamical spin-lattice interaction as the dominant effects in determining the fast and moderate temporal evolution of the carrier relaxation process. The similar temperature dependence of these two interactions suggests a magnetic-electric coupling in multiferroic BiFeO_3 , which is inferred to be the in-plane strain and magnetic-elastic

coupling. The dynamical coupling and the optical control of either magnetism, ferroelectricity, or both in BiFeO_3 have implications for future ultrafast optical-electronic devices.

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