Article

Element Selected Spin-Dependent d-d Charge Transfer Transitions in $\text{Bi}_2\text{FeMnO}_6$ Film: An Ultrafast Pump-Probe Study

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Featured Application: The ultrafast electron-phonon and spin-lattice coupling process in multiferroic films could give new insight into the optical microscopic measuring in condense matter physics.

Abstract: The ultrafast optical response of the magnetic compound $\text{Bi}_2\text{FeMnO}_6$ (BFMO) is studied through 100–300 K by means of ultrafast transient reflectivity spectroscopy. By using differing pump energy, the optical low spin (LS) transition and high spin (HS) transition in this compound are distinguished as the temperature varies. This charge transfer transition is shown to be spin-dependent and element selected. The ultrafast spin-lattice coupling time also shows the element selected feature, which illustrated the two independent magnetic phase transitions to the antiferromagnet (AFM) Mn–O–Mn and the ferrimagnet (FIM) Mn–O–Fe order, respectively.

Keywords: ultrafast optics; optics materials; ultrafast spectroscopy; multiferroic

1. Introduction

Multiferroic materials possess spontaneous electric and magnetic order which offers integration possibilities for multiple functionalities in a single material [1,2]. Particularly, multiferroics open a new venue for controlling the magnetism by applied electrical field through magneto-electric coupling at room temperature, and vice versa [3,4]. However, the G-type anti-ferromagnetic form and the incommensurate spin cycloid structure makes the electric-magnetic coupling rarely weak in bismuth ferrite [5]. BiMnO_3 shows ferromagnetic order and ferroelectric order below 100 K [6]. Therefore, the mixing compound $\text{Bi}_2\text{FeMnO}_6$ drew much concern in recent years [7–9]. The reduced Néel temperature, the complicated exchange coupling between Fe and Mn ions and the G-type antiferromagnetic structure, which differs from BiFeO_3 and BiMnO_3 , have shown the enormous novel physical properties of this compound [10–13].

The electronic properties in condensed matters directly show their physical properties. The interplay among the electron, lattice and spin degrees of freedom in multiferroic and other correlated electron materials can be studied in the time domain by ultrafast spectroscopy [14,15]. The ultrafast d-d transfer blue shift is found in YMnO_3 which shows the connection between the d-electron charge

transfer band gap and the macroscopic magnetism in multiferroics [16]. The low-temperature phase transition of BiFeO₃ is revealed by transient reflectivity, which shows the underlying magnetic-lattice coupling in bismuth ferrite [17]. The role of the double exchange mechanism in their magnetism's origin and the magneto-electric coupling of LuFe₂O₄ is revealed by transient reflectivity in the vicinity of the Néel temperature [18]. Therefore, the d-d charge transfer rate is quite sensitive to the magnetism, which could be used to study the underlying d-electron structure and magnetism in Bi₂FeMnO₆. For the single B site multiferroics, the pump-probe technique is widely used; however, the hybrid 3d transition element in B sites have been seldom investigated, which could show spectrum selectivity. In this letter, we report the temperature dependent, ultrafast charge transfer in Bi₂FeMnO₆/Si film, a compound of d-electron materials. The 1.55 eV transition is attributed to the Mn³⁺ d-d charge transfer, and the 3.1 eV transition is attributed to dominate by way of the d-d transition between the antiferromagnetic Fe³⁺ ions. The temperature dependent transition probability of d-d charge transfer in Fe³⁺ and Mn³⁺ could be attributed to the temperature dependent correlations between Mn spins and between Fe spins, respectively. These behaviors indicate the transition probability in Bi₂FeMnO₆ differs between the two transitions by high-spin and low-spin transitions [19]. The spin-lattice coupling process is also shown to be element dependent, which is related to the Mn–O–Fe and Mn–O–Mn ordering temperatures, respectively.

2. Materials and Methods

The well crystallized single-phase Bi₂FeMnO₆ film was deposited on a silicon substrate using a pulsed laser deposition method (PLD) at 923 K with 500–600 mTorr dynamic oxygen. The film thickness was about 150 nm. The reflection-type absorption spectra were measured in UV-3600, (Shimadzu Corporation, Kyoto, Kyoto Prefecture, Japan), with a relative type suite. A reflection type pump probe set up was employed here which was described in detail in formal lectures [17]. The light source was provided by a commercial mode-locked Ti:sapphire laser (Spitfire Pro, Spectra-Physics, CA, USA) running at the 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 was obtained from a frequency-doubled fundamental beam (800 nm) in a 1 mm β-BaB₂O₄ crystal. The average pump fluence was about 6 mJ/cm² which is 30 times larger than that of the probe. Both of the pump and probe beams were focused on the surface of the sample with a spot diameter about 200 μm. The sample was mounted in a closed-cycle liquid-He cryostat in vacuum chamber with four optically accessible windows.

By altering the doping ratio, x , between 0 and 1, the band gap for BiFe _{x} Mn _{$1-x$} O₃ could be modulated from 1.2–2.6 eV [12]. Figure 1a shows the reflection type UV-Vis spectrum of Bi₂FeMnO₆/Si film. It could be seen from Figure 1 that two distinct reflectivity dips occur at 1.1 eV and 1.5 eV, respectively. The 1.1 eV dip arises from the band gap transition of silicon substrate, and the higher energy dip at 1.5 eV corresponds to the on-site Mn³⁺ d-d charge transfer (CT) gap at room temperature, which is consistent with reported values of the band gap at $x = 0.5$ in the literature [9,12]. The other slight deviations correspond to the mechanical error for changing optical gate. Figure 1b shows the transition processes of electrons in the corresponding materials by 1.55 eV pumping and 3.1 eV pumping, respectively. In perovskite manganite the 1.55 eV transition is determined to be the e_g-t_{2g} transition which is $\Gamma^3 \rightarrow \Gamma^5$ between the hybridized O²⁻(2p)-Mn³⁺(3d) states and the Mn³⁺ states [16,19–21].

Figure 1. (a) The reflection spectrum of Bi₂FeMnO₆ film. A reflection spectrum of Si was used as a reference, and the sample signal is multiplied by 5 times for a visual guide. (b) Schematically shows the electronic band structure of Bi₂FeMnO₆.

3. Results and Discussion

Figure 2a shows the 1.55 eV pump-probe signal of Bi₂FeMnO₆ (BFMO) and its temperature dependence. It is different from the nonlinear two-photon absorption of BiFeO₃ with a 1.55 eV pump described elsewhere. The signal of the sample is negative and proportional to the pump power, so they represent the charge transfer transition probabilities of 1.55 eV and 3.1 eV for Bi₂FeMnO₆ samples, respectively [22].

Figure 2. (a) The time resolved ΔR of Bi₂FeMnO₆ film with a 1.55 eV pump and 1.55 eV probe setup. The vertical direction is shift with equal magnitude for clarity. (b) The time resolved ΔR of Bi₂FeMnO₆ film with 3.1 eV pump and 1.55 eV probe setup, the vertical direction is shift with equal magnitude for clarity.

A convolution of the Gaussian pulse $G(t)$ with a bi-exponential decay function is utilized to analyze the electron dynamics phenomenologically,

$$\Delta R = \left[A_1 \exp\left(-\frac{t}{\tau_{e-ph}}\right) + A_2 \exp\left(-\frac{t}{\tau_{s-ph}}\right) + A_3 \right] \otimes G(t) \quad (1)$$

where A_1 and A_2 are the amplitudes of the fast and slow components mentioned above, respectively. τ_{e-ph} and τ_{s-ph} are the relaxation time constants of the electron-phonon and spin-lattice interactions, respectively. A_3 is a flat background, which recovers to the ground state after a much longer time delay (hundreds of picoseconds–several nanoseconds) [17]. Figure 2b shows the temperature dependent 3.1 eV pump, 1.55 eV probe time resolved reflectivity. For the 1.55 eV pump, the peak ΔR signal increased gradually when the temperature decreased from 290 K to 120 K, which is similar to the blue shift effect of d-d transition energy gap in YMnO_3 thin film material [23]. The blue-shift of the absorption band with the temperature is related to the emergence of the magnon and the optical phonon side bands, the emergence of the phonon side bands results in the effect of the temperature-dependent shift of the absorption band [24]. For 3.1 eV pumping, the peak ΔR signal decreases with the decrease of temperature, which is similar to that of d-d transition signal in LuFe_2O_4 sample with the change of Néel temperature [18]. Therefore, the corresponding transition of 3.1 eV and 1.55 eV in $\text{Bi}_2\text{FeMnO}_6$ samples corresponds to the d-d transition of different element ions.

The negative response of the transient reflectivity shows optically induced absorption behavior of both the 1.55 eV and the 3.1 eV pump scenarios. Thus, the instantaneous reflectivity represents the excited state population of the carriers. Figure 3a shows the temperature dependent reflectivity values at zero delay time for both 1.55 eV and 3.1 eV pump pulses. Figure 3b shows the temperature dependent magnetization of the film, which indicated that the total sample magnetization become stronger when the temperature went down. From the $d(M/H)/dT$ signal, which is the derivative of the $(M/H)/T$ signal of the film, which is sensitive to the magnetic phase transition temperature. It can be concluded that with the decrease of temperature, two magnetic phase transition processes took place. The phase transition temperatures of 200 K and 150 K are considered to correspond with the ordered phase transition of the Fe–O–Mn ferromagnetic phase and Mn–O–Mn antiferromagnetic phase respectively [8]. The ordered temperature of Fe–O–Fe is 440 K. The possible reasons for the magnetic phase transition are the random distribution of elements in the lattice, the growth environment of the sample and the strain induced by the substrate [8]. It can be seen from Figure 3a that when the pump light is 1.55 eV, the amplitude at zero time delay increases with temperature, which corresponds to the increase of charge transfer transition probability of Mn^{+3} ions. Because of Hund's rule, the transition probability of this single particle charge transfer transition under the influence of spin interactions can be divided into two series, high-spin transition and low-spin transition [19]. As the name implies, high-spin (HS) transition means that the total spin number of ions increases after charge transfer transition, and the corresponding spectral weight is $S_1 S_2 S \rightarrow S_1 \pm \frac{1}{2} S_2 \mp \frac{1}{2} S$. Low-spin (LS) transition, $S_1 S_2 S \rightarrow S_1 - \frac{1}{2} S_2 - \frac{1}{2} S$, means that the total spin number of ions decreases after charge transfer [16]. For B site Mott insulators, the dependence of low and high spin transitions on temperature is opposite, so 1.55 eV and 3.1 eV correspond to two different transitions [25]. For the Fe^{3+} ion-based oxides we deal only with the LS transitions $\frac{5}{2} \frac{5}{2} \rightarrow 22$; therefore, the 1.55 eV pump for the Mn^{3+} d-d transition is corresponding to the HS transition, which means that the temperature dependent energy shift in manganite should be related to the spin structure [16]. The evolution of the spin structure could be reflected in the ions' optical properties if their magnetism is connected with their electronic properties. Therefore, we can expect that the spectral weight transfer is strongly correlated to the magnetic phase transition for each 3d cation configuration, which is wavelength selected in $\text{Bi}_2\text{FeMnO}_6$ compounds. A possible origin of the difference that could be considered is their different exchange energy. The absorption of a 1.55 eV photon creates a pair of Mn^{2+} and Mn^{4+} ions for the short range ordered Mn cations. The blue shift for the spectral weight transfer for the 3.1 eV pump indicates that the creation of Fe^{2+} and Fe^{4+} ions are suppressed for the increasing of the super-exchange interaction

intensity. The low-spin transition is dominated in this Fe 3d charge transfer transition because of the Fe–O–Fe configuration and the anti-ferromagnetic structure. Thus, the charge transfer transition in $\text{Bi}_2\text{FeMnO}_6$ for 3.1 eV is dominated by the d-d transition for the Fe 3d cation, which is also sensitive to the Néel temperature in other ferrites such as LuFe_2O_4 [18].

Figure 3. (a) The amplitude of the negative peak ($|R_0|$) as a function of temperature. The red dotted line shows the temperature dependence of ΔR peak of 1.55 eV pump corresponding to the d-d transition for Mn, and the blue dotted line shows the temperature dependence of ΔR peak of 3.1 eV pump corresponding to the d-d transition for Fe. We note that the error bars are comparable to the size of the data points and are therefore not shown. (b) The $d(M/H)/dT$ curve for the $\text{Bi}_2\text{FeMnO}_6$ film.

The interpretation of different degrees of freedom in $\text{Bi}_2\text{FeMnO}_6$ are also consisted with the complicated phase transitions. As it's shown in Figure 4a,b, the temperature is dependent on the time constant of the electron-phonon coupling and the spin-lattice coupling process. Except the enhancement of the magnetization as shown in Figure 3b, there are two apparent transitions in the $d(M/H)/dT$ curve of the sample. Although the electro-phonon interaction time varies slightly with the temperature, it does not change abruptly with the phase transition temperature. It indicates that the structure and ferroelectric properties of $\text{Bi}_2\text{FeMnO}_6$ samples do not change when the magnetic properties of the samples change [16]. The temperature dependence of spin-lattice coupling time under 3.1 eV pumping and 1.55 eV pumping is obviously different. For 1.55 eV pumping, the slow process occurs at the Mn–O–Mn antiferromagnetic order temperature of 240 K, indicating that the interaction between the magnetic order and the lattice occurs. While at 175 K, ferromagnetic phase transition temperature of Fe–O–Mn changes from >10 ps to about 5 ps, which indicates that the interaction intensity between spin and lattice increases with the increase of magnetic ordering in Mn. For the 3.1 eV pumping case, the spin lattice coupling time τ_{s-ph} does not change significantly at 240 K, indicating that the relaxation process of d-d transition in Fe^{+3} ions at this temperature does not exchange heat with the spin in Mn^{+3} ions. When the temperature decreases to 175 K, the spin lattice coupling time τ_{s-ph} disappears, which indicates that the spin lattice coupling process disappears. The spin interaction is enhanced when the magnetic structure of BFMO changes from Fe–O–Fe antiferromagnetic phase to Fe–O–Mn ferromagnetic phase. Therefore, the dependence of slow process time on temperature can further prove the complex magnetic ordered phase transition between B site ions in BFMO samples [26–28].

Figure 4. (a) The temperature dependence of the fast component $\tau(\text{fast})(\text{ps})$ (τ_{e-ph}) for different pump wavelengths; the blue for 3.1 eV and red for 1.55 eV pumps, respectively. (b) The temperature dependence of the slow component $\tau(\text{slow})(\text{ps})$ (τ_{s-ph}) for different pump wavelengths. Both diagrams have highlighted the two magnetic phase transition ranges for guiding eyes.

4. Conclusions

In summary, we have presented an optical pump-probe study of the multiferroic Bi₂FeMnO₆/Si film. For the spectral difference between Fe and Mn cations, the 1.55 eV and 3.1 eV charge transfer transition is determined to be the Mn³⁺ 3d and the Fe³⁺ 3d charge transfer transition, respectively. Meanwhile, the temperature dependent spin-lattice coupling time both for Mn-3d and Fe-3d electron was extracted. Their behavior is consistent with the two magnetic phase transitions in BFMO film, the ferrimagnet (FIM) Mn–O–Fe order at 175 K and the Mn–O–Mn AFM order at 250 K, respectively. The element selected pumping of the ultrafast carrier dynamics in BFMO film gave rise to the new insights of the optical investigation and manipulation of the B site doping magnets or other perovskite correlated electron systems.

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