Ultrafast Control of the Polarity of BiCoO_{3} by Orbital Excitation as Investigated by Femtosecond Spectroscopy

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Ultrafast Control of the Polarity of $BiCoO_3$ by Orbital Excitation as Investigated by Femtosecond Spectroscopy

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Abstract

$BiCoO_3$ is a perovskite-type cobalt oxide with a polar structure. We investigated dynamics of its polar state by using photoexcitation with femtosecond visible and THz pulses. The intensity of the second harmonic light, caused by a polar structure without inversion symmetry, was enhanced by more than 50% by irradiating the THz pulse showing ultrafast response following the fs THz pulse. In contrast, it was suppressed by more than 60% by exciting visible light with 100fs pulse width at room temperature. These results suggest not only an important role of the orbital excitation in the Co^{3+} ion but also a key to improving the nonlinear optical response, *e.g.*, a figure of merit in nonlinear crystals on the time scale of femtosecond.

I. INTRODUCTION

Solid materials with a polar structure have attracted much interest in condensed matter physics because the polar materials including ferroelectrics show various interesting mechanical, electrical, and optical phenomena originating from the breaking of inversion symmetry. Among them, second-order nonlinear optical phenomena (such as second harmonic (SH) generation, photovoltaic effect, and generation of THz pulses) are also attractive in the light of photonic materials science as well as basic research on ferroelectric systems. As is widely known, there are two keys to observing the nonlinear effects: finite second-order electric susceptibility $\chi^{(2)}$ originating from the polar structure, and strong laser light or pulses.

For the past few decades, the development of ultrafast laser systems has not only enabled us to easily access the optical nonlinear properties but also revealed the importance of the photoexcited state driven by the fs laser light [1]. Many studies concerning the photoinduced state have been reported especially in strongly correlated materials as well as semiconductors, demonstrating various ultrafast control of the refractive index or absorption coefficient by light. Such photoirradiation can also control nonlinear optical properties originated from $\chi^{(2)}$ [2,3] in addition to the refractive index. This indicates the possibility that the figure of merit of nonlinear materials can optically be improved via the nonequilibrium state, and hence it is important toward future applications in nonlinear optical devices to search for materials showing gigantic and ultrafast change of the second order effect driven by the increase of $\chi^{(2)}$ by light.

Among many examples of the strongly correlated oxides, perovskite-type cobalt oxides are known to show a unique variation of the spin configuration coupled with the lattice and electronic structures, which is called a spin crossover (SC) phenomenon [4]. The SC change is a spin state transition of the trivalent Co(III) ion in a CoO_6 octahedron between low spin (LS; t_{2g}^6) and high spin (HS; $t_{2g}^4 e_g^2$) state. The origin of the SC is basically attributed to the energy balance between Hund's rule coupling and the crystal field splitting, though other scenarios exists such as an intermediate spin (IS; $t_{2g}^5 e_g^1$) state stabilized by the dynamical

Jahn-Teller effect [5]. An important point of the SC Co oxide system is that the SC change can also be realized by applying various external stimuli, such as changing temperature [4], applying a strong magnetic field [6], and irradiating light [7–9].

Lately, Azuma *et al*. reported a new class of SC cobaltite, $BiCoO_3$ (BCO) [10]. Figure 1(a) shows the crystal structure of BCO at room temperature. The crystal symmetry is P4mm. Unlike a typical perovskite, there is one apical oxygen shift along the *c*-axis and a Co-O_5 pyramid exists in the unit cell. This clearly suggests that BCO has a polar structure as a result of the symmetry breaking along the *c*-axis, which gives birth to gigantic spontaneous polarization about $\approx 120\mu$C/cm at room temperature [10]. In BCO, both the Bi and Co ions are trivalent and the spin configuration of Co^{3+} is a HS state due to the pyramidal structure, where the degenerated e_g and t_{2g} states are lifted as depicted in Fig. 1(b) [10]. An important aspect of BCO is the pressure effect: applying external pressure can change the spin configuration in Co^{3+} from the HS state to a lesser spin state (the IS or LS state) with the lattice contraction [10]. They also revealed that the pressure induced SC change was involved in the polar to nonpolar structural change, indicating that BCO belongs to not only the SC family but also a new class of a strongly correlated polar material, which is an attractive target for future applications in ferroelectric devices.

In this paper, we report ultrafast control of the nonlinear behavior in the polar SC cobaltite BCO using fs visible and terahertz (THz) laser pulses as external perturbations. For the THz pulse, a technique has recently been developed [11] that can generate a strong electromagnetic wave that has an electric field that reaches up to an order of ≈ 1 MV/cm in the THz photon energy region. Such an intense electric field has recently enabled us to see intriguing phenomena driven by such a strong field: the dynamical Frantz-Keldish effect in semiconductors [12,13], insulator-metal phenomena in an correlated oxide [14,15], and photoinduced superconductivity [16]. In this report, using the THz pulses and novel polar cobaltite, we demonstrate large and ultrafast enhancement of the SH signal by more than 50% and discuss its origin in terms of orbital excitations in Co^{3+}, referring to the recently proposed idea of a photon-dressed state [17–19]. The observed results can be viewed as an

optical technique not only to cause ultrafast switching of $\chi^{(2)}$ but to enhance the value of $\chi^{(2)}$ itself in polar materials.

II. EXPERIMENT

A polycrystalline sample of BCO was fabricated under a high pressure of ≈ 6 GPa at 1200°C, the details of which are described elsewhere [10]. The surface of the pressed sample for the following optical measurements was prepared by polishing using alumina slurries. The relative changes in reflectivity ($\Delta R/R$) and SH intensity [20] ($\Delta I_{\rm SH}/I_{\rm SH}$) after the optical pumping of visible and THz pulses were obtained by using the conventional pump-probe method using a mode-locked Ti sapphire laser light with a regenerative amplifier system (≈150 fs pulse width, 1 kHz repetition rate, and ≈1.55 eV photon energy). The amplified light was separated into two light beams. We used one beam as a probe pulse to detect the reflectance and SH change. In the reflectance measurement, the reflected light was detected by semiconductor photodiodes, and in SH measurement, the frequency doubled light (≈3.1 eV) was detected by a photomultiplier through the high-pass filters and the grating-type monochromator to cut the fundamental ≈1.55 eV pulses as shown in Fig. 1(c).

For the photoexcitation, we used two different pulses: a visible pulse (≈2.6 eV) converted by an optical parametric amplifier, and a THz pulse generated by the tilted pulse front method using a $LiNbO_3$ crystal. The details of the generation process of the THz pulse are described elsewhere [11]. The temporal profile of the THz pulse was detected by an electro-optical sampling method. The generated THz pulse was focused onto the sample by using a parabolic mirror as shown in Fig. 1(c). All the experiments were done in air and at room temperature.

III. RESULTS AND DISCUSSIONS

Figure 2(a) shows delay time (t_d) dependence of $\Delta R/R$ at 0.25 and 0.8 eV. The fluence of the pump light (480 nm) is ≈8.2 mJ/cm^2. In both the photon energies, $\Delta R/R$ shows a

sudden jump just after the photoirradiation. The open circles denote the fitting result at 0.8 eV using a single exponential and a constant term, indicating that the lifetime is ≈ 0.2 ps. The inset shows the transient spectrum just after the photoexciation. The reflectance spectrum of $BiCoO_3$ is flat reflecting the insulating behavior, but, just after the photoexcitation, the reflection around the near-infrared region forms a broad peak, suggesting the appearance of a hidden electronic state. Very recently, Ishihara *et al*. theoretically calculated the photoexcited state for cobaltite, which is characterized by the near-infrared peak due to the trapped e_g electrons via the double exchange interaction (HS polaron state) [21]. This explanation is very consistent with the observed transient spectrum in BCO.

Figure 2(b) shows time dependence of $\Delta I_{\rm SH}/I_{\rm SH}$. In contrast to $\Delta R/R$, $\Delta I_{\rm SH}/I_{\rm SH}$ suddenly decreases by 60% with the pumping of $\approx$8.2 mJ/cm^2. This indicates the pump light decreased the averaged value of polarizations of the embedded polar domains. After the sudden decrease, $\Delta R/R$, $\Delta I_{\rm SH}/I_{\rm SH}$ similarly decays in the case of $\Delta R/R$, the decay time of which is also estimated as ≈ 0.2 ps. One scenario to explain the results is suppression of the binding energy of the crystal of BCO. The pumping light causes the charge-transfer (CT) excitation from O $2p$ to Co $3d$ orbital [4], which reduces the total Madelung energy. This might weaken the stiffness of the metastable polar structure of the cobalt oxide. Consequently, the photoexcited state in BCO by the visible light pumping is characterized by two results: the near-infrared peak formed due to the HS polaronic state, and the SH intensity greatly suppressed due to the photogeneration of the less polar structure.

The next issue to be highlighted is THz pulse excitations in BCO. Figure 3(b) shows temporal profiles of the applied THz field ($E_{\rm THz}$) used for the pump light. In the orange, green, and blue profiles, intensities of the field were 3/4, 1/2, and 1/4 that in the red profile, respectively. (The ringing structures after 1 ps in the temporal profile are caused by water vapor absorption in air.) In the red profile, the maximum value of the peak field ($E^{\rm peak}$) was $\approx$0.8 MV/cm at $\approx$0 ps.

Figure 3(a) shows time dependence of $\Delta I_{\rm SH}/I_{\rm SH}$ of BCO with irradiation of the THz pulses shown in Fig. 3(b). In stark contrast to the photoexcitation case (Fig. 2), by applying

E_{THz}, $\Delta I_{\mathrm{SH}}/I_{\mathrm{SH}}$ clearly increases, and the magnitude of the relative change exceeds 50 % at $t_d \approx 0$ in the red profiles. As the E_{THz} decreases, $\Delta I_{\mathrm{SH}}/I_{\mathrm{SH}}$ decreases nonlinearly. What should be noted is the sign of $\Delta I_{\mathrm{SH}}/I_{\mathrm{SH}}$. In BCO, $\Delta I_{\mathrm{SH}}/I_{\mathrm{SH}}$ is always positive, regardless of the direction of the THz pulse. It is worth noting that whereas the large change in $\Delta I_{\mathrm{SH}}/I_{\mathrm{SH}}$, $\Delta R/R$ scarcely varies ($< 0.1\%$) with the THz field [22]. This signals that the applied field is barely affected by the linear refractive index or absorption coefficient at 3.1 eV and hence the change of $\Delta I_{\mathrm{SH}}/I_{\mathrm{SH}}$ cannot originate from the photonic change of the first order of the electric susceptibility, $\chi^{(1)}$.

In Fig 4, to see the variation of the SH change more quantitatively, we plotted the normalized maximum value ($\Delta I_{\mathrm{SH}}^{\mathrm{peak}}$) at ≈0 ps as a function of the peak electric field, E^{peak}. The value of $\Delta I_{\mathrm{SH}}^{\mathrm{peak}}$ nonlinearly increases as E^{peak} increases. The E^{peak} dependence of the $\Delta I_{\mathrm{SH}}^{\mathrm{peak}}$ is well fit by the parabolic curve as shown by the solid line. The inset of Fig. 4 demonstrates the time profile of $\Delta I_{\mathrm{SH}}/I_{\mathrm{SH}}$ (black circles) together with that of $|E_{\mathrm{THz}}|^2$ (red line). $\Delta I_{\mathrm{SH}}/I_{\mathrm{SH}}$ is well scaled by $|E_{\mathrm{THz}}|^2$. These results signal the observed SH change is proportional to $|E_{\mathrm{THz}}|^2$ at all t_d. It is interesting to compare the result with that in an organic ferroelectrics, TTF-CA by Miyamoto *et al*. [2]. They also observed that the SH intensity is modulated by applying the THz pulse, in which the value of $\Delta I_{\mathrm{SH}}/I_{\mathrm{SH}}$ is proportional to E_{THz} in TTF-CA, implying that E_{THz} slightly modulates the direction of the polarization. This is in contrast to the observed change in BCO, where $\Delta I_{\mathrm{SH}}/I_{\mathrm{SH}} \propto |E_{\mathrm{THz}}|^2$.

Here, let us discuss an origin of the observed THz field effect. Our results show the positive increase of I_{SH} regardless of the direction of E_{THz}, suggesting that the THz pulse affects $\chi^{(2)}$ itself through the optical transition by the THz pulse. Very recently, Iwai *et al*. [23] has demonstrated that some absorption peaks originate from the *d*–*d* transition through a quadrupole or magnetic dipole process around the THz energy region, where the usual optical phonons are not observed in a similar perovskite $LaCoO_3$ [24]. Judging from the spin configuration in Fig. 1(b), in BCO, it is reasonable to consider that the *d*–*d* excitation from an occupied d_{xy} to an unoccupied d_{yz} or d_{zx} state can exist around the wide energy band of an applied THz pulse. Under these circumstances, the photoexcited d_{yz} or d_{zx} electron can

further elongate the apical oxygen of the pyramid thorough electron-phonon coupling and hence cause the resultant enhancement of the pyramidal polar structure or increase of $\chi^{(2)}$. When we take the lowest term of E_{THz}, $\chi^{(2)}$can be expanded [25] as $\chi^{(2)} \approx \chi_0^{(2)} + \Delta\chi^{(2)}|E_{\mathrm{THz}}|^2$, where $\chi_0^{(2)}$ and $\Delta\chi^{(2)}$ are the original susceptibility and variation of $\chi^{(2)}$ with the THz pulse, respectively. Then, $\Delta I_{\mathrm{SH}}/I_{\mathrm{SH}} \approx 2|\Delta\chi^{(2)}/\chi_0^{(2)}||E_{\mathrm{THz}}|^2$, which is consistent with the observed power dependence in Fig. 4.

In this scenario of the actual orbital excitation, however, one may consider that the disappearance of $\Delta I_{\mathrm{SH}}/I_{\mathrm{SH}}$ in Fig. 3(a) without a THz field is difficult to explain because the lattice deformation might remain even after the THz field is removed. Very recently, Morimoto and Nagaosa have calculated $\chi^{(2)}$ in ferroelectrics [18,19] taking account of the dressed state as well as Berry phase connections between the valence and conduction bands. According to their results, the value of $\chi^{(2)}$ can be enhanced as long as the incident light forms photon dressed excitons in the ferroelectric crystal. This idea can be one scenario for our THz experiment: the interorbital transition between t_{2g} states driven by THz pulse can cause an exitonic THz-dressed state, which can explain not only the resultant increase of $\chi^{(2)}$ but also the observed ultrafast change of I_{SH}. This model is one of the possible candidates and to make clear the microscopic mechanism a more detailed approach needs to be studied and developed for the photoexcited state considering fourth current response with pumping light and the incident pulse, in addition to the ultrafast structural measurement with THz pulse.

IV. SUMMARY

In summary, we investigated the photoexcited state and variation of the SH generation effect in a polar cobalt perovskite, BCO by pumping femtosecond visible and THz pulses. Whereas the 480 nm excitation suppressed the SH intensity by $\approx 60\%$, irradiating the THz pulse (≈ 0.8 MV/cm^2) largely enhanced the SH intensity by more than 50 % on the time scale of fs at room temperature. Especially the ultrafast enhancement of the SH signal might

be understood in terms of the photonically dressed orbital transitions between Co t_{2g} states driven by the THz pulse as recent theoretical work has suggested. These results can propose a technique to control the nonlinearity, or χ^2 of a polar material by light on the fs timescale. The irradiation of THz pulse can be viewed as a method for optically improving figure of merit in nonlinear crystals for fs laser pulses.

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REFERENCES

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†† present address: Faculty of science and engineering, Chuo University, 1-13-27, Kasuga, Tokyo, 112-8551, Japan.

[1] As a comprehensive review, Photoinduced Phase Transitions, edited by K. Nasu (World Scientific publishing, Singapore, 2004).

[2] T. Miyamoto, H. Yada, H. Yamakawa, and H. Okamoto, Ultrafast modulation of polarization amplitude by terahertz fields in electronic-type organic ferroelectrics, Nature com. **4**, 2586 (2013).

[3] H. Yamakawa, T. Miyamoto, S. Watanabe, Y. Shimoi, M. Suda, H. M. Yamamoto, H. Mori and H. Okamoto, Novel electronic ferroelectricity in an organic charge-order insulator investigated with terahertz-pump optical-probe spectroscopy, Sci. Rep. **6**, 20571 (2015), S. Iwai *et al.*, unpublished.

[4] For example, M. Imada, A. Fujimori, and Y. Tokura, Metal-insulator transitions, Rev. Mod. Phys. **70**, 1039 (1998).

[5] M. A. Korotin, S. Y. Ezhov, I. V. Solovyev, V. I. Anisimov, D. I. Khomskii, and G. A. Sawatzky, Intermediate-spin state and properties of $LaCoO_3$, Phys. Rev. B **54**, 5309 (1996).

[6] K. Sato, A. Matsuo, K. Kindo, Y. Kobayashi, and K. Asai, Field induced spin-state transition in $LaCoO_3$, J. Phys. Soc. Jpn. **78**, 093702 (2009), A. Ikeda, T. Nomura, S. Takeyama, Y. H. Matsuda, A. Matsuo, K. Kindo, and K. Sato, Spin state ordering of strongly correlating $LaCoO_3$ induced at ultrahigh magnetic fields Phys. Rev. B **93**, 220401(R) (2016).

[7] Y. Okimoto, X. Peng, M. Tamura, T. Morita, K. Onda, T. Ishikawa, S. Koshihara, N. Todoroki, T. Kyomen, and M. Itoh, Ultrasonic propagation of a metallic domain in $Pr_{0.5}Ca_{0.5}CoO_3$ undergoing a photoinduced insulator-metal transition, Phys. Rev. Lett. **103**, 027402 (2009).

[8] Y. Okimoto, M. Kurashima, K. Seko, T. Ishikawa, K. Onda, S. Koshihara, T. Kyomen, and M. Itoh, Acceleration of domain wall movement by photoirradiation in perovskite-type cobaltite, Phys. Rev. B **83**, R161101 (2011).

[9] Y. Okimoto, T. Miyata, M.S. Endo, M. Kurashima, K. Onda, T. Ishikawa, S. Koshihara, M. Lorenc, E. Collet, H. Cailleau, and T. Arima, Ultrafast spectral weight transfer in $R\mathrm{BaCo_2O_{6-\delta}}$ (R = Sm, Gd, and Tb): Role of electronic correlation in a photoinduced phase transition, Phys. Rev. B **84**, R121102 (2011).

[10] K. Oka, M. Azuma, W. Chen, H. Yusa, A.A. Belik, E. T. Muromachi, M. Mizumaki, N. Ishimatsu, N. Hiraoka, M. Tsujimoto, M. G. Tucker, J. P. Attfield, and Y. Shimakawa, Pressure-induced spin-state transition in $BiCoO_3$, J. Am. Chem. Soc. **132**, 9438 (2010).

[11] H. Hirori, A. Doi, F. Blanchard, and K. Tanaka, Single-cycle terahertz pulses with amplitudes exceeding 1 MV/cm generated by optical rectification in $LiNbO_3$, Appl. Phys. Lett. **98**, 091106 (2011).

[12] H. Hirori, M. Nagai, and K. Tanaka, Excitonic interactions with intense terahertz pulses in ZnSe/ZnMgSSe multiple quantum wells, Phys. Rev. B **81**, 081305 (2010).

[13] K. Shinokita, H. Hirori, M. Nagai, N. Satoh, Y. Kadoya, and K. Tanaka, Terahertz-induced optical emission of photoexcited undoped GaAs quantum wells, Appl. Phys. Lett. **97**, 211902 (2010).

[14] M. Liu, H. Y. Hwang, H. Tao, A. C. Strikwerda, K. Fan, G. R. Keiser, A. J. Sternbach, K. G. West, S. Kittiwatanakul, J. Lu, S. A. Wolf, F. G. Omenetto, X. Zhang, K. A. Nelson, and R. D. Averitt, Terahertz-field-induced insulator-to-metal transition in

vanadium dioxide metamaterial, Nature **487**, 345 (2012).

[15] K. Itoh, H. Itoh, M. Naka, S. Saito, I. Hosako, N. Yoneyama, S. Ishihara, T. Sasaki, and S. Iwai, Collective excitation of an electric dipole on a molecular dimer in an organic dimer-Mott insulator, Phys. Rev. Lett. **110**, 106401 (2013).

[16] M. Mitrano, A. Cantaluppi, D. Nicoletti, S. Kaiser, A. Perucchi, S. Lupi, P. Di Pietro, D. Pontiroli, M. Ricco, S. R. Clark, D. Jaksch and A. Cavalleri, Possible light-induced superconductivity in K_3C_60 at high temperature, Nature **530**, 461 (2016).

[17] N. Tsuji, T. Oka, P. Werner and H. Aoki, Dynamical band flipping in fermionic lattice systems: an ac-field-driven change of the interaction from repulsive to attractive, Phys. Rev. Lett. **106**, 236401 (2011).

[18] T. Morimoto and S. Nagaosa, Topological nature of nonlinear optical effects in solids, Sci. Adv. **2**, e1501524 (2016).

[19] T. Morimoto and S. Nagaosa, Topological aspects of nonlinear excitonic processes in noncentrosymmetric crystals, Phys. Rev. B **94**, 035117 (2016).

[20] In the polycrystalline sample, the directions of the polarized domains may be randomly embedded, and we observed SH intensity proportional to the square of the incident probe light, because the averaged dipole moment existed in the macroscopic probed area $\approx 100\mu m$ in diameter.

[21] Y. Kanamori, H. Matsueda, and S. Ishihara, Photoinduced change in the spin state of itinerant correlated electron systems, Phys. Rev. Lett. **107**, 167403 (2011).

[22] Y. Okimoto and H. Hirori, unpublished.

[23] S. Iwai *et al.*, unpublished.

[24] S. Yamaguchi, Y. Okimoto, and Y. Tokura, Local lattice distortion during the spin-state transition in $LaCoO_3$, Phys. Rev. B **55**, R8666 (1997).

[25] In the expansion, the term proportional to E_{THz} originated from the ultrafast modulation of the averaged polarization of domains is finite in BCO. However, we neglected it because the E_{THz}-linear term is expected to be even smaller than the observed $|E_{\mathrm{THz}}|^2$ term in BCO as shown in Fig. 4 [2].

FIGURES

FIG. 1. The crystal structure (a) and the spin configuration (b) of $BiCoO_3$ after Ref.[10]. (c): Schematics of the THz pump and SHG probe measurement system, in which M, L, and HPS are mirror, lens and high-pass filter, respectively. The THz pump pulse was focused onto the sample using the parabolic mirror while the 800 nm probe pulse with the lens through the parabolic mirror. The generated SH pulse was introduced to the monochromator and detected by the photomultiplier.

FIG. 2. Delay time (t_d) dependence of relative change of the reflectivity ($\Delta R/R$) at 0.25 eV and 0.8 eV (a) and second harmonic intensity ($\Delta I_{\rm SH}/I_{\rm SH}$) (b) after photoirradiation of $\approx$ 2.6 eV pulse. The inset shows the transient reflectance spectrum just after the photoirradiation ($t_d \approx 0$ ps). The fluence of the pump pulse is $\approx$8.2 mJ/cm^2.

FIG. 3. (a): Time profiles of the relative change of the second harmonic intensity ($\Delta I_{\rm SH}/I_{\rm SH}$) with several different THz pulse. The color of each profile corresponds to that of THz pulse shown in (b). (b): Waveforms of the THz filed used for the photoexcitation in the time domain. In the orange, green, and blue profiles, intensities of the field were 3/4, 1/2, and 1/4 that in the red profile, respectively.

FIG. 4. Normalized maximum value of the second harmonic change at $\approx$ 0 ps ($\Delta I_{\rm SH}^{\rm peak}$) as a function of the peak value in the THz electric field ($E^{\rm peak}$). Inset shows time profiles of $\Delta I_{\rm SH}/I_{\rm SH}$ and square of the applied THz field ($|E_{\rm THz}|^2$).

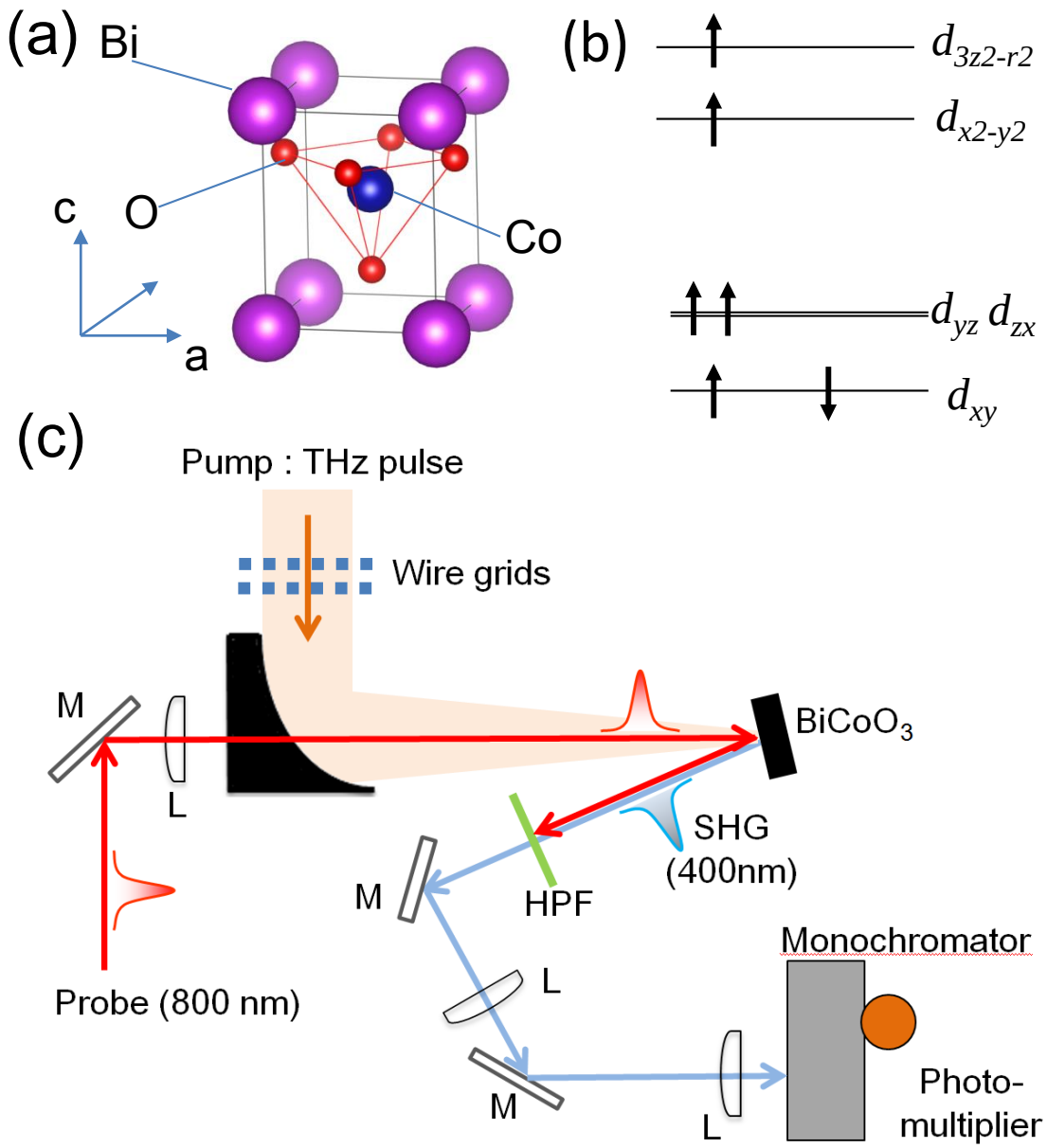

Fig. 1 Okimoto et al.

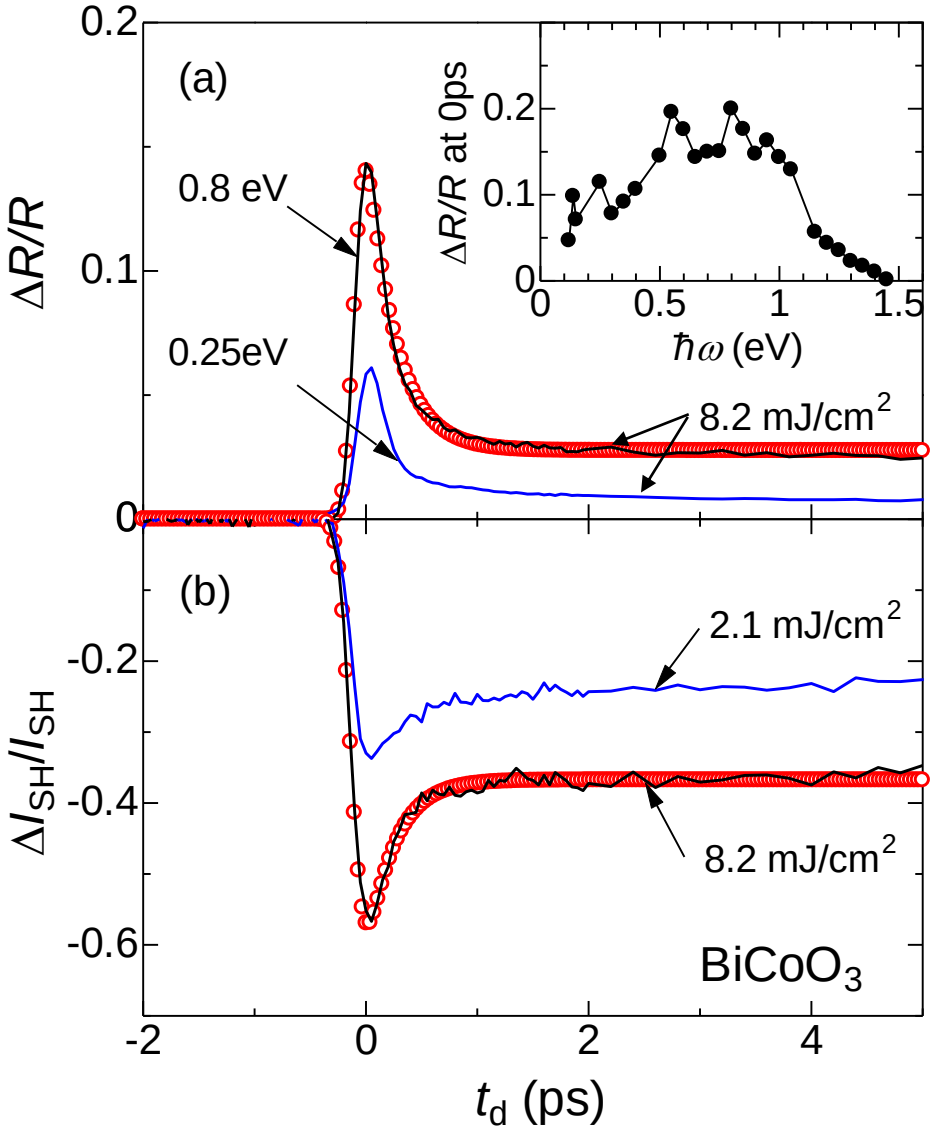

Fig. 2 Okimoto et al.

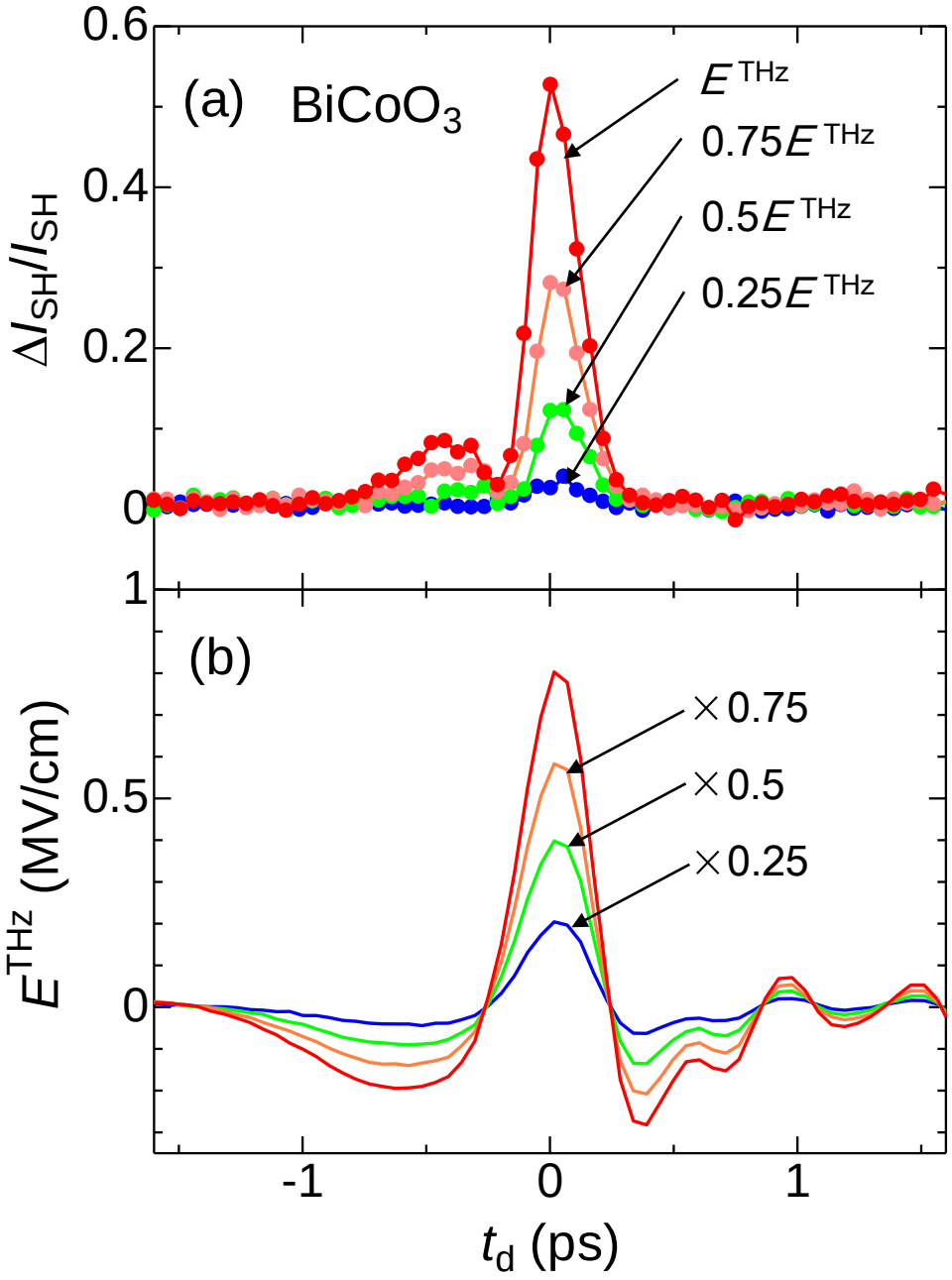

Fig. 3 Okimoto et al.

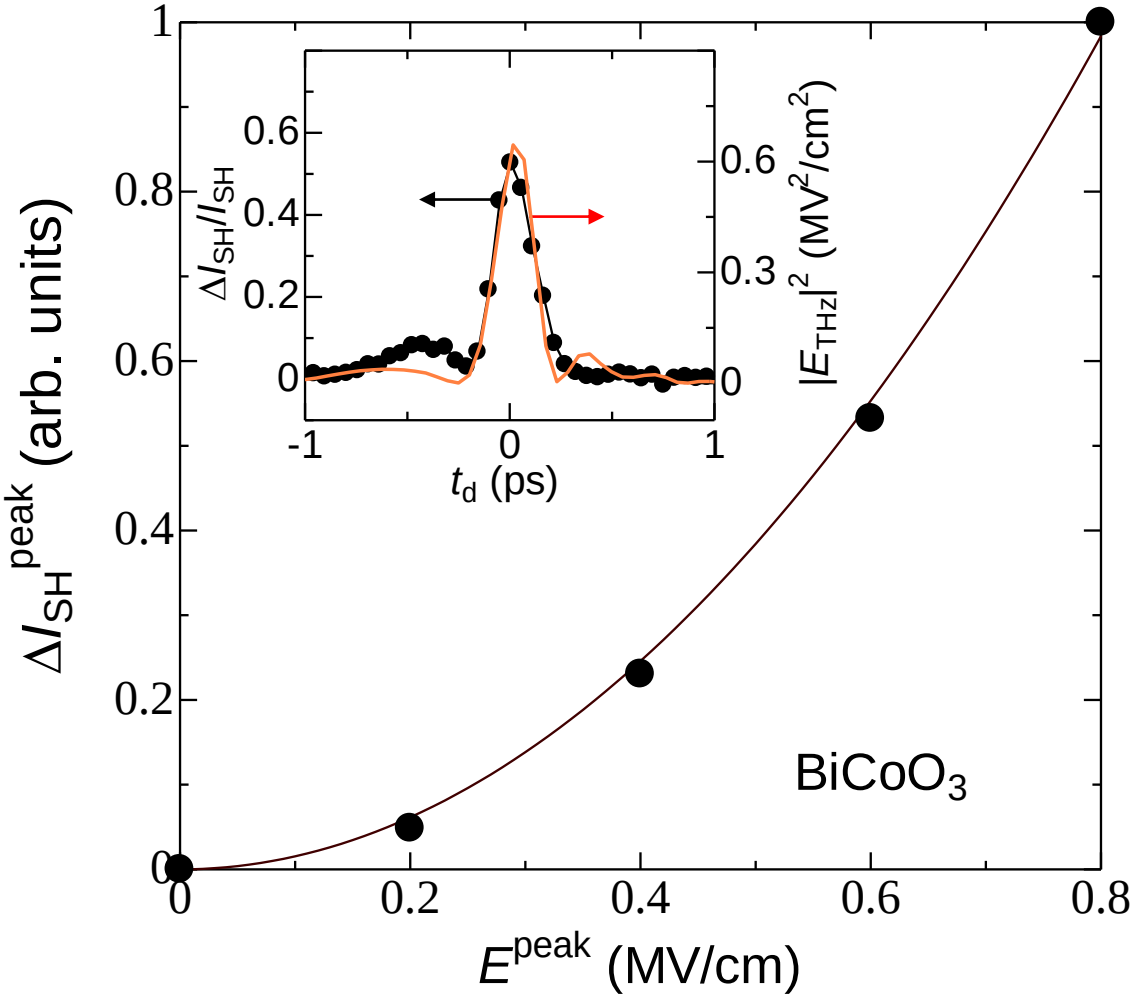

Fig.4 Okimoto et al.