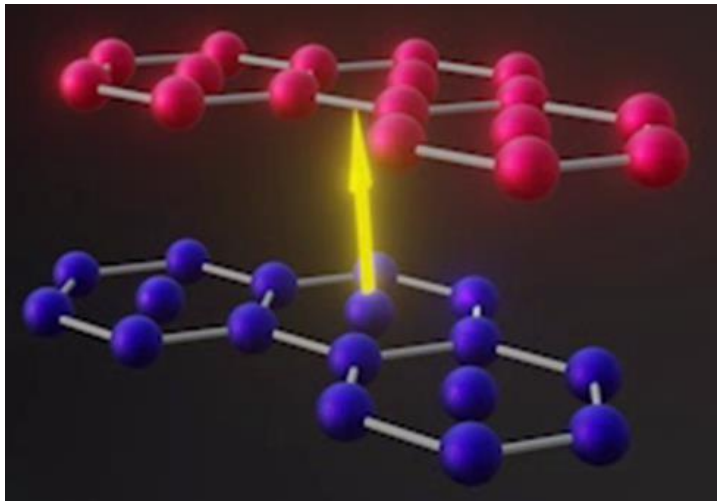
Ultrafast anisotropic polarization dynamics of electronic ferroelectrics, $R\mathrm{Fe_2O_4}$

Tokyo Institute of Technology
Yoichi Okimoto



Acknowledgments

Tokyo Tech. H. Yu, S. Wang, A. Sugisawa, T. Ishikawa, S. Koshihara

Okayama Univ. N. Inoue, Y. Fukada, N. Ikeda, T. Sakagami, R. Ohta, T. Fujii

QST K. Fujiwara

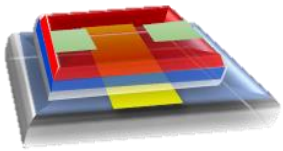
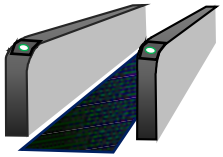
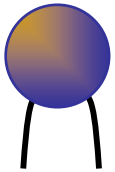
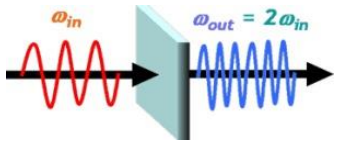
Tohoku Univ. H. Itoh and S. Iwai

ISSP, Univ. Tokyo R. Fukaya and J. Itatani

Ferroelectrics

1. Polar structure (no inversion symmetry)
2. Polarization reversal by electric field

Applications for RAM, actuator, capacitance, etc…

The development of exotic ferroelectrics is important.

⇒ Research target: electronic ferroelectrics

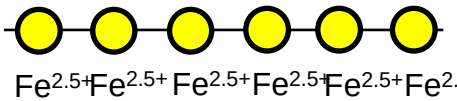
Electronic ferroelectrics (EF)

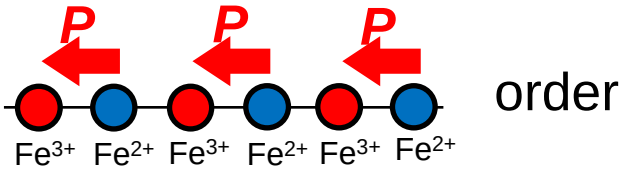
What's EF?

✔Electron ordering
✔A role of electron correlation
cf. S. Ishihara, *JPSJ*. (2010).

What's the merit of EF?
→ Reversal of the polarization with Lower voltage?
Ultrafast response?

An example of 1D iron crystal composed of Fe^{2+} and Fe^{3+}





Polarization occurs by the order of electrons without shift of ions!

Candidates

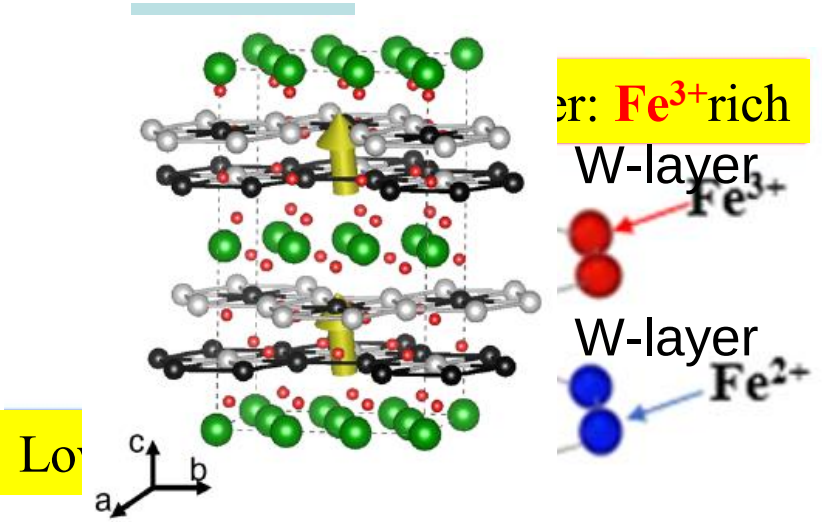
Organic crystals:
- $(TMTTF)_2X$ Monceau *et al*., PRL (2001).
- α-$(BEDT\text{-}TTF)_2I_3$ Yamamoto, Iwai *et al*., JPSJ (2008).

Inorganic iron oxide:
- **$LuFe_2O_4$** N. Ikeda *et al*., Nature **436**, 1136 (2005).

1. Polarization Structure

✔$LuFe_2O_4$ (Fe^{2+} : Fe^{3+}=1:1) N. Ikeda *et al*., Nature **436**, 1136 (2005).

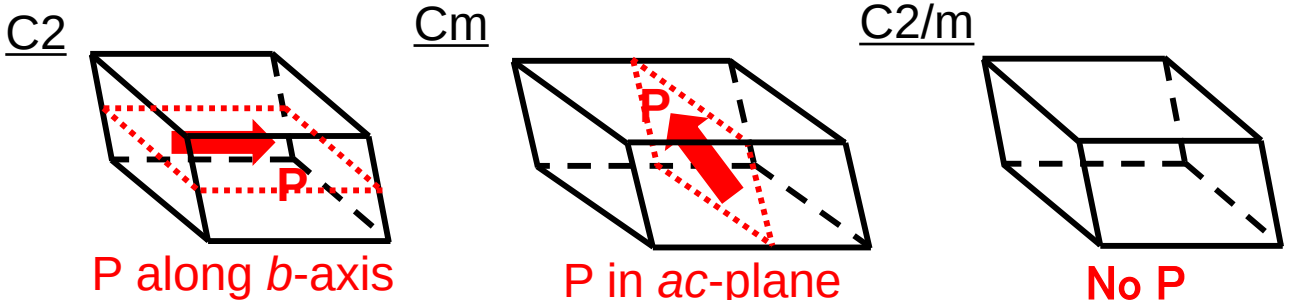
In the W-layer, Fe^{2+} and Fe^{3+} ions exhibit a threefold periodic alignment.



The W-layer is composed of Fe^{3+}-rich and Fe^{2+}-rich sheet.
⇒Polarization along the c-axis!

👉Diffraction measurement suggests…

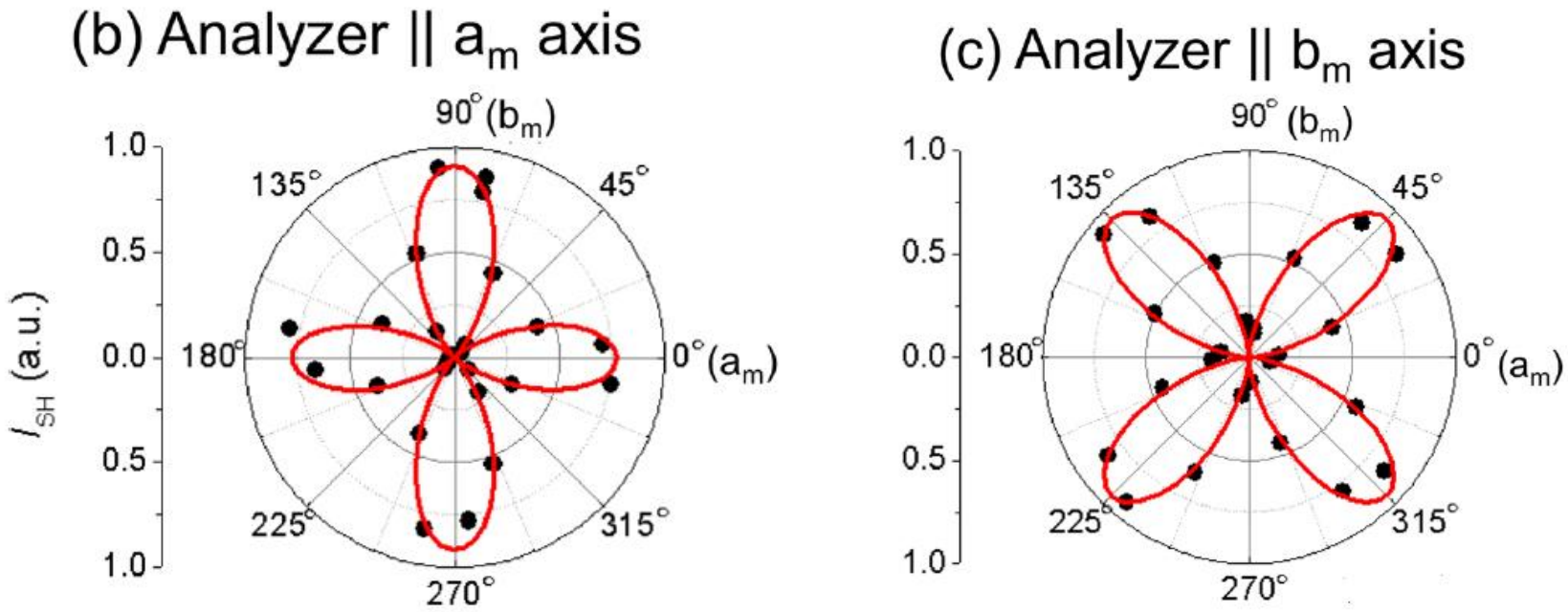
K. Fujiwara *et al.*, *Ferroelectrics* **512**, 85 (2017)



Monoclinic

Polarization Structure

ab surface



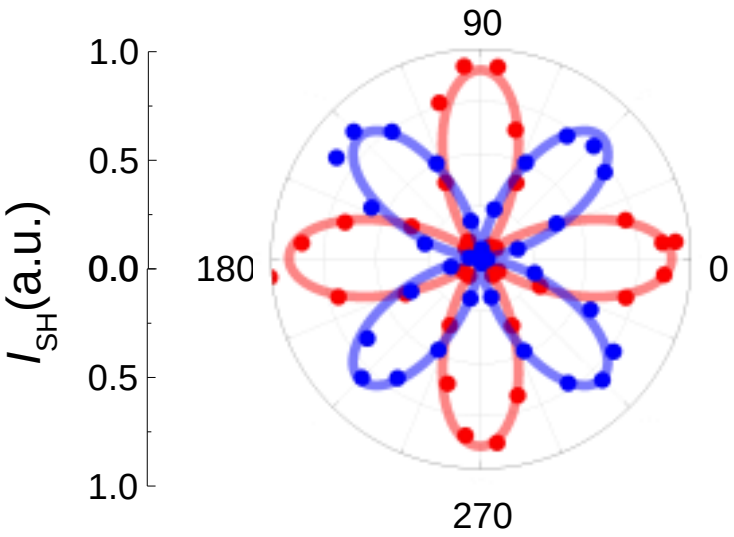
$YbFe_2O_4$

K. Fujiwara, **Y.O.**, *et al.*, *Sci. Rep.* ***11***, 4277 (2021).

- ✓ **SHGs are observed, indicating the polar structure.**
- ✓ **A strong fs laser pulse is indispensable. (No signal with ns pulses)**
- ✓ **Azimuth angle dependence reflects the polarization structure.**

Polarization Structure

$LuFe_2O_4$ *ab* surface



analyzer || a

analyzer || b

In the point group of Cm…

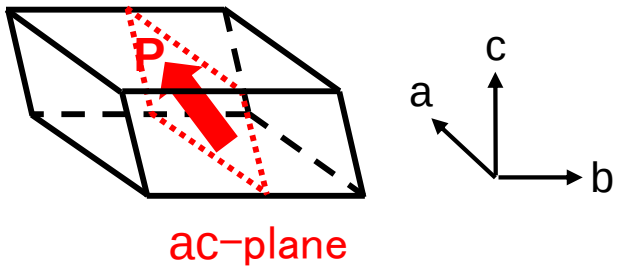
$$I^{SH}{}_a \propto |P^{(2)}|^2 \propto |d_{11}\cos\theta + d_{12}\sin\theta|^2$$

$$I^{SH}{}_b \propto |P^{(2)}|^2 \propto |d_{26}|^2 \sin^2 2\theta$$

$\chi^{(2)}$ **Monoclinic *Cm***

$$\begin{pmatrix} d_{11} & d_{12} & d_{13} & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & d_{26} \\ d_{31} & d_{32} & d_{33} & 0 & d_{35} & 0 \end{pmatrix}$$

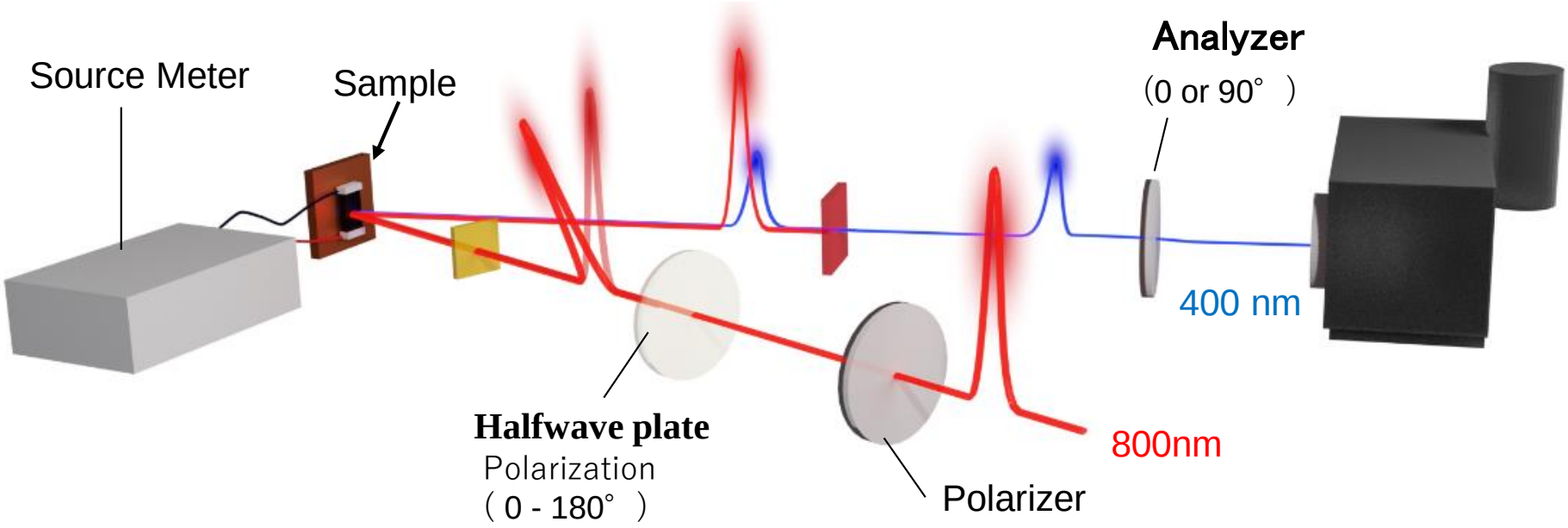
Cm



K. Fujiwara, Y.O., *et al.*, *Sci. Rep.* ***11***, 4277 (2021).

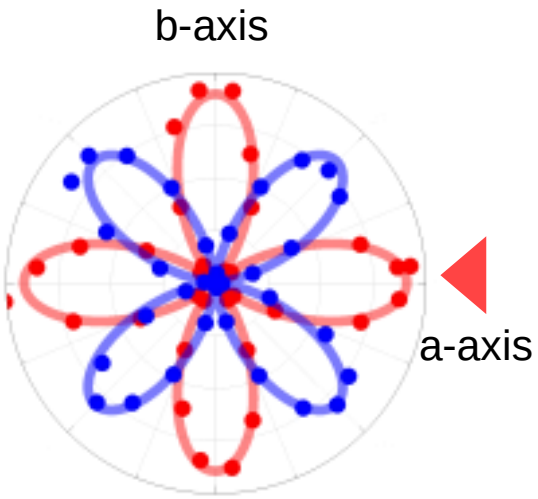
2. Can the polarization be reversed?

✔ Electric field dependence of SHG

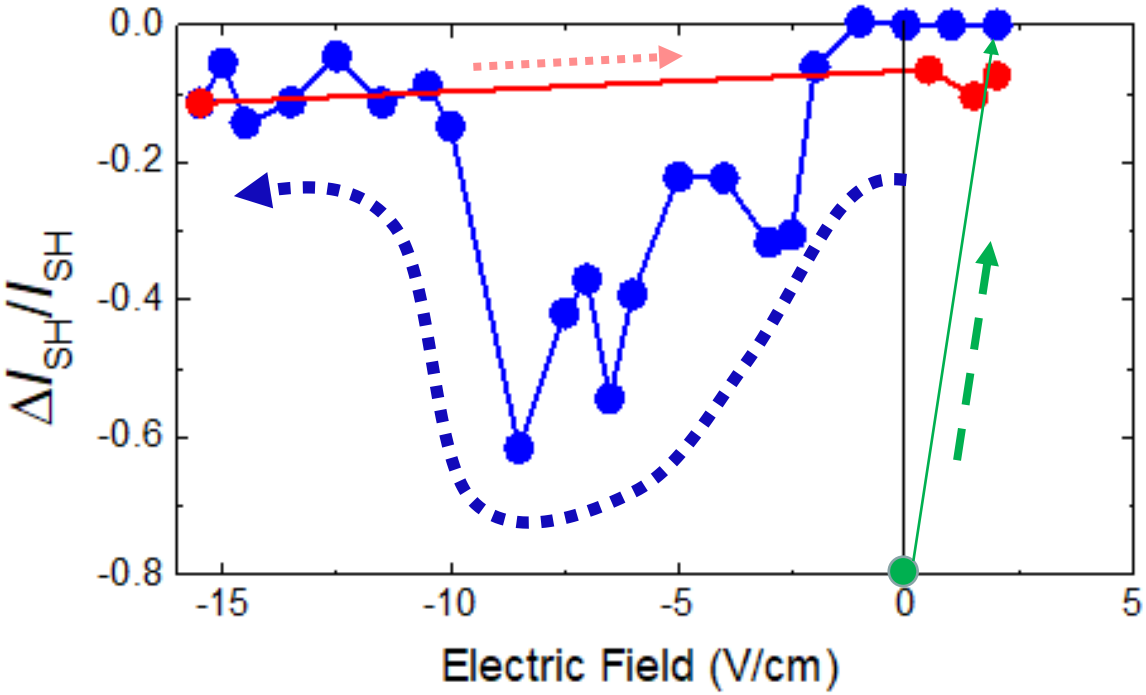


In the *ab* plane, an electric field is applied in the *a*-axis direction, and the field dependence of the emitted 400 nm SHG is measured.

Can the polarization be reversed?



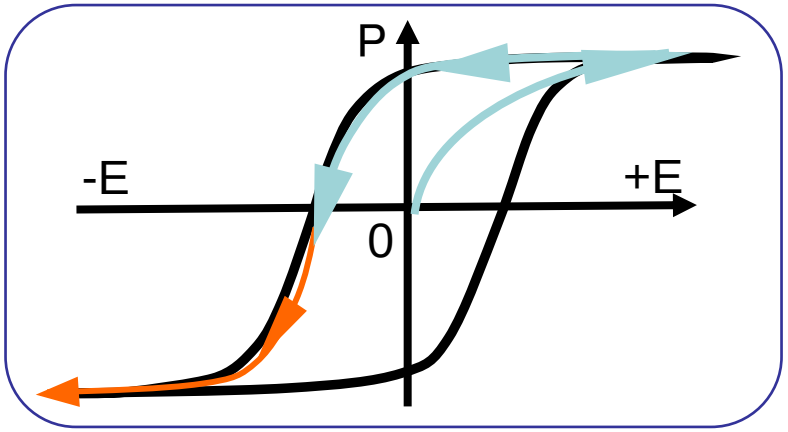
Analyzer || a-axis



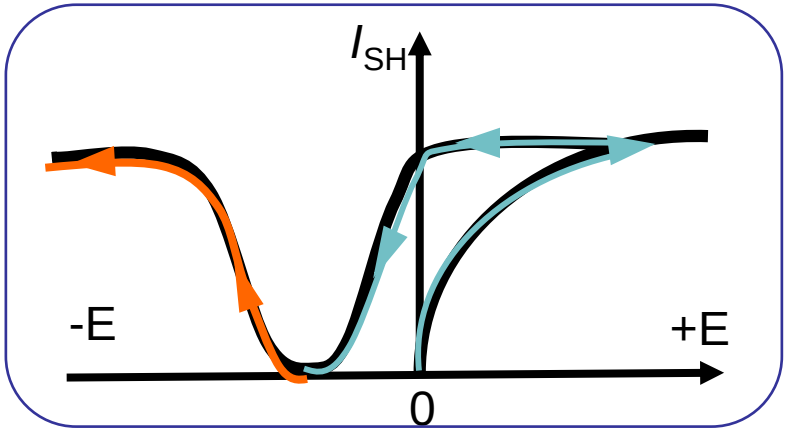
1. As the electric field is applied, the polarization is aligned and the SHG value increases.
2. When the electric field is reversed, a reentrant variation is observed at around <10 V/cm.

The origin of the reentrant behavior in SHG

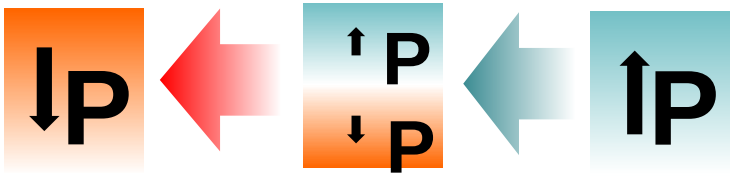
P-E loop in a usual FE



E-dependence of SHG



SHG is proportional to P^2



1. As the electric field is applied, P is aligned and SHG increases.
2. When the electric field is reversed, SHG shows a reentrant variation.

Polarization can be reversed with the field less than～10 V/cm.

In PZT, the coersive field is ～1 kV/cm.

Ultrafast response（d-d transition）

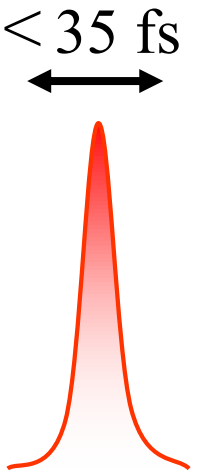
Phys. Rev. Mat. **8**, 064402 (2024)

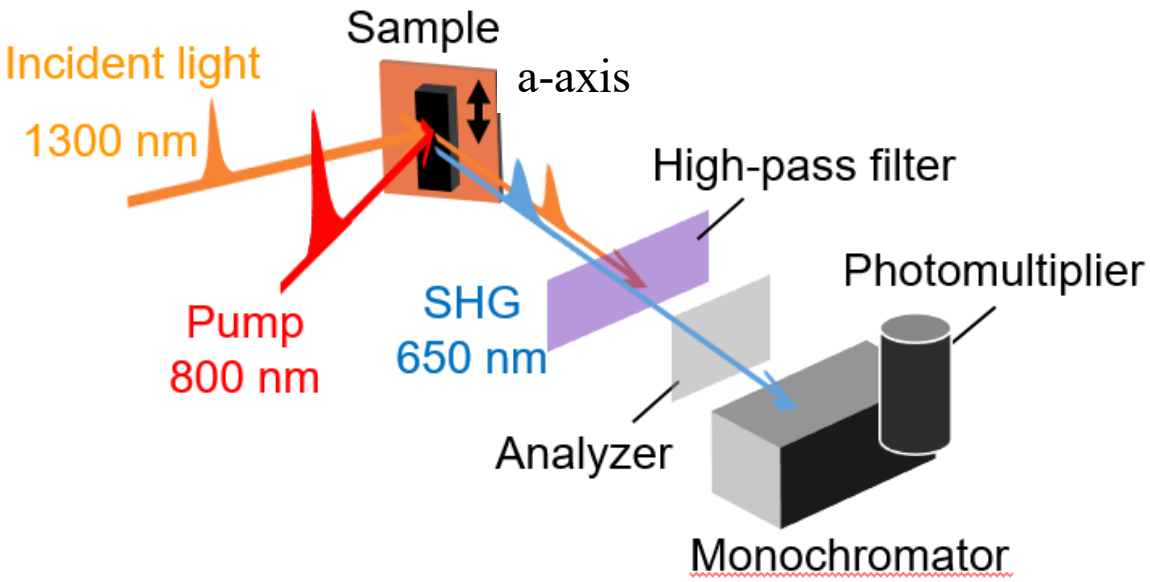
1． Pump-probe SHG measurements with 35 fs pulses

✓With photoexcitation of 800nm pulse….

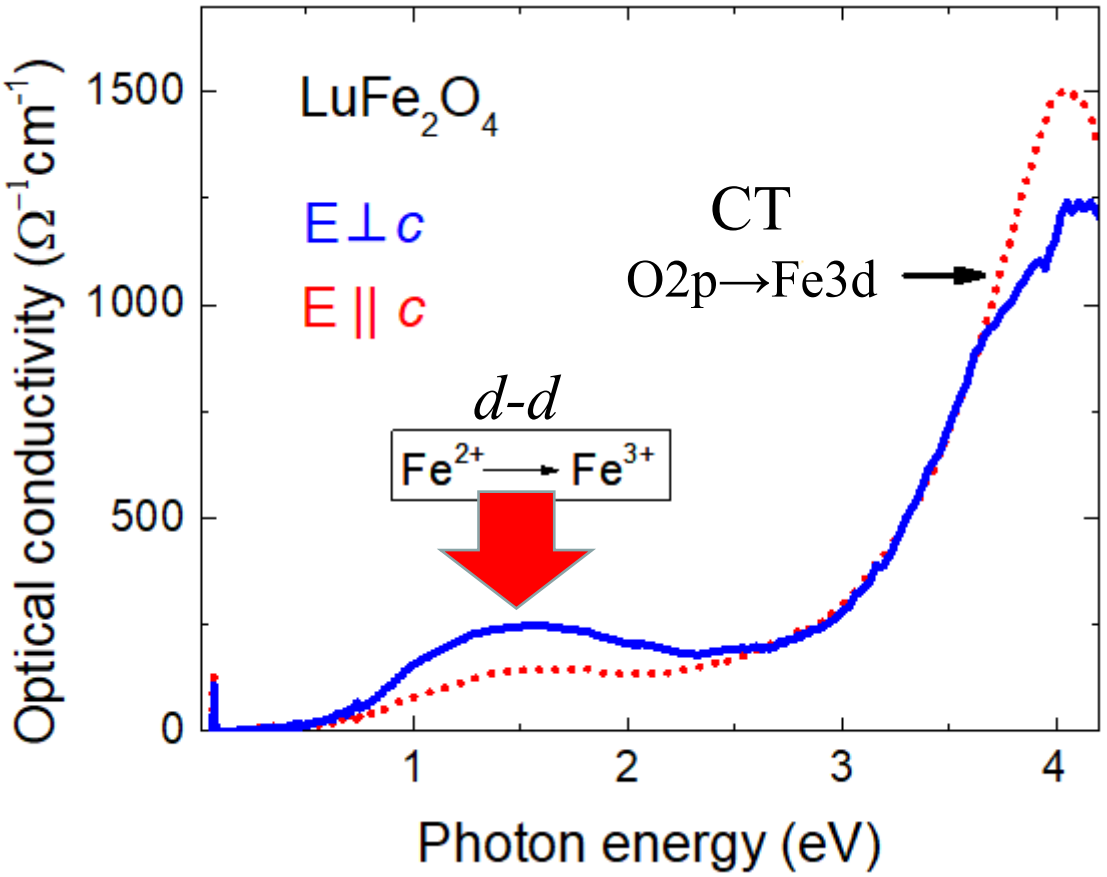
→ *d-d* transition between the iron sites

→ With the destruction of the iron order, what happens in the SHG?





Electronic structure of $LuFe_2O_4$

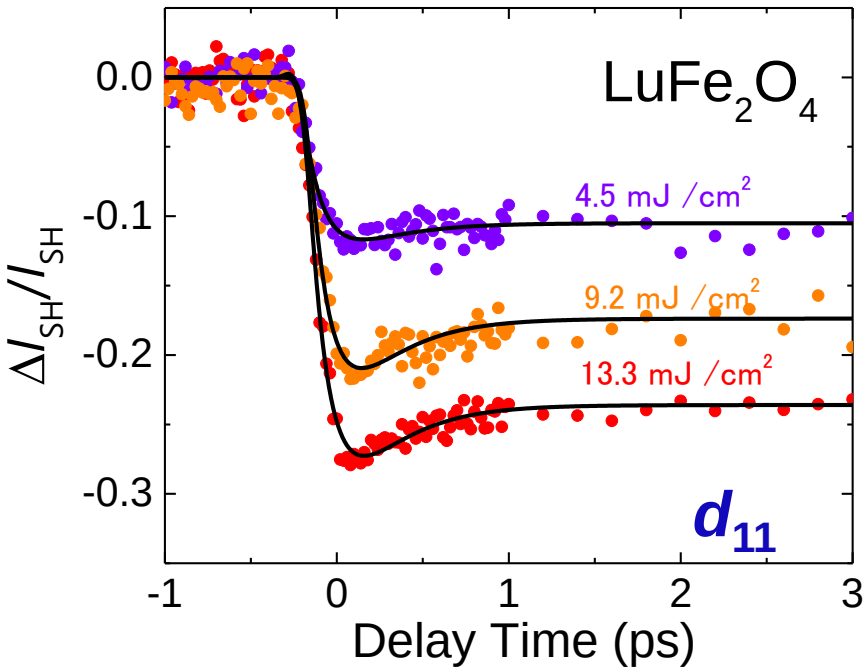


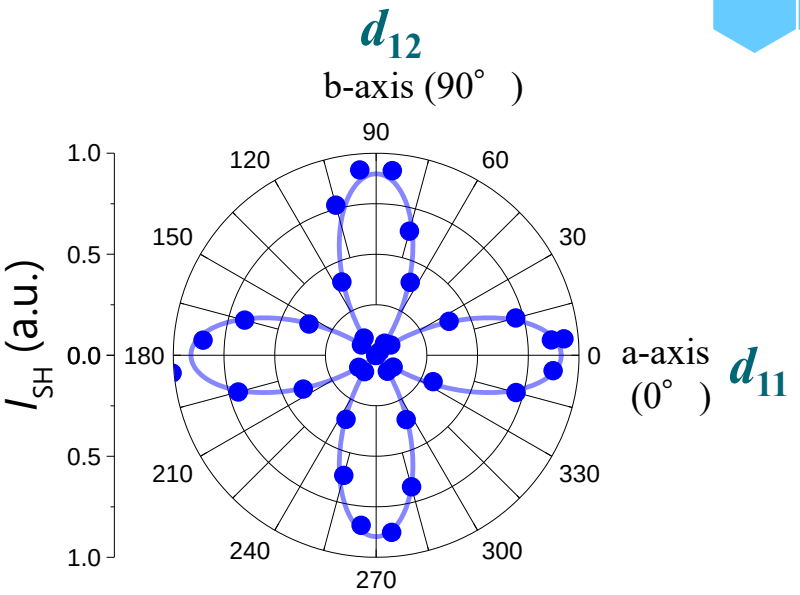
Optical conductivity has two broad peaks..
Intersite *d-d* transition at ～1.5 eV and CT peak above 3eV

→ The 800nm pulse can excite Fe *d-d* transition.

Dynamics in the *ab*-plane

$LuFe_2O_4$





✓ SHG intensity was reduced by up to 30%.

（**Instant suppression of the polarity**）

✓ Slight relaxation and long-lived state were observed.

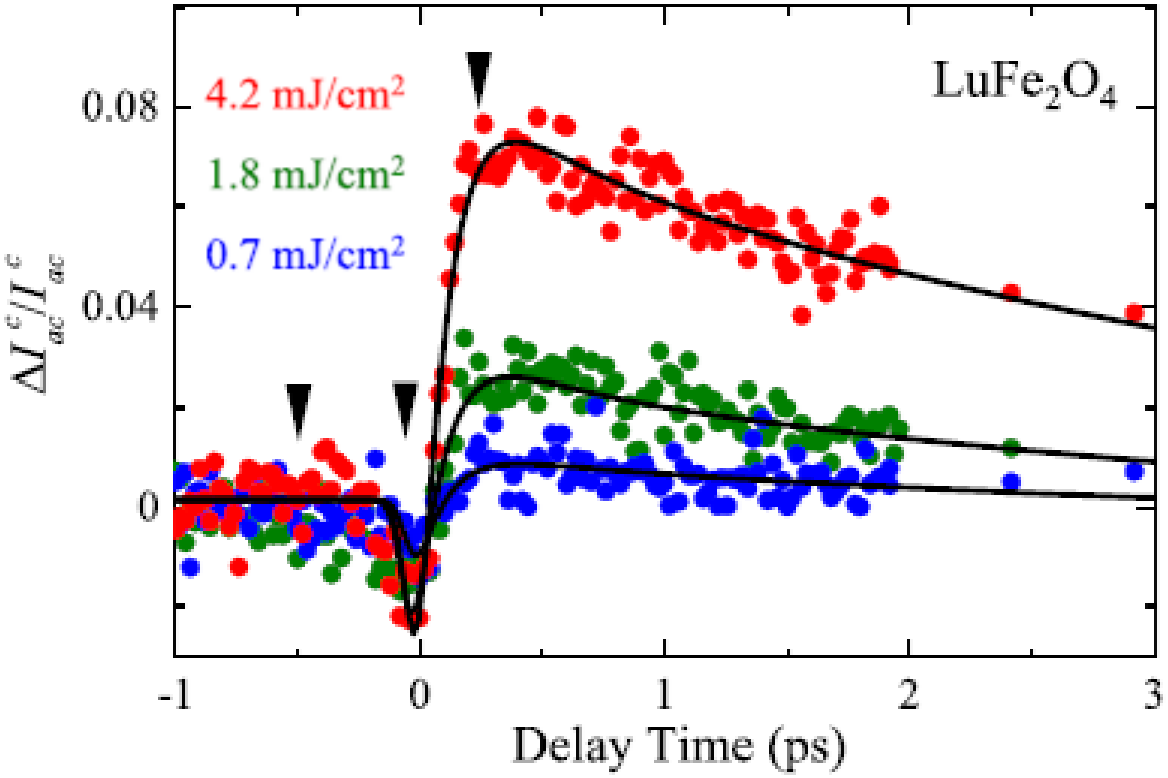
$$f(t) = -A_1\left\{1 - exp\left(-\frac{t-t_0}{\tau_1}\right)\right\} + A_2\, exp\left(-\frac{t-t_0}{\tau_2}\right) + \mathrm{B}$$

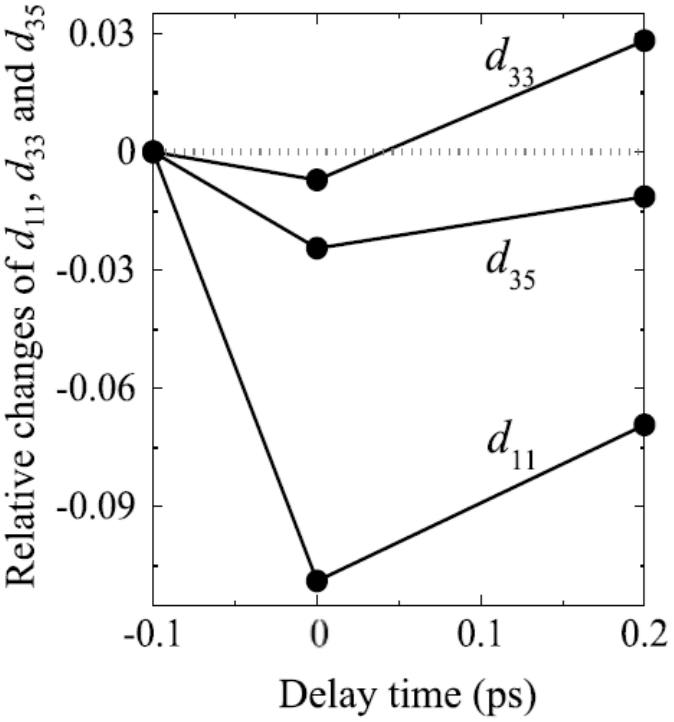
τ_1 = 0.12 ps、 τ_2 = 0.29 ps

→*Suppression of d_{11}*, indicating disorder of charge order in *ab*-plane

Dynamics in *ac*-plane

$LuFe_2O_4$





✓ Variation of SHG ∥c

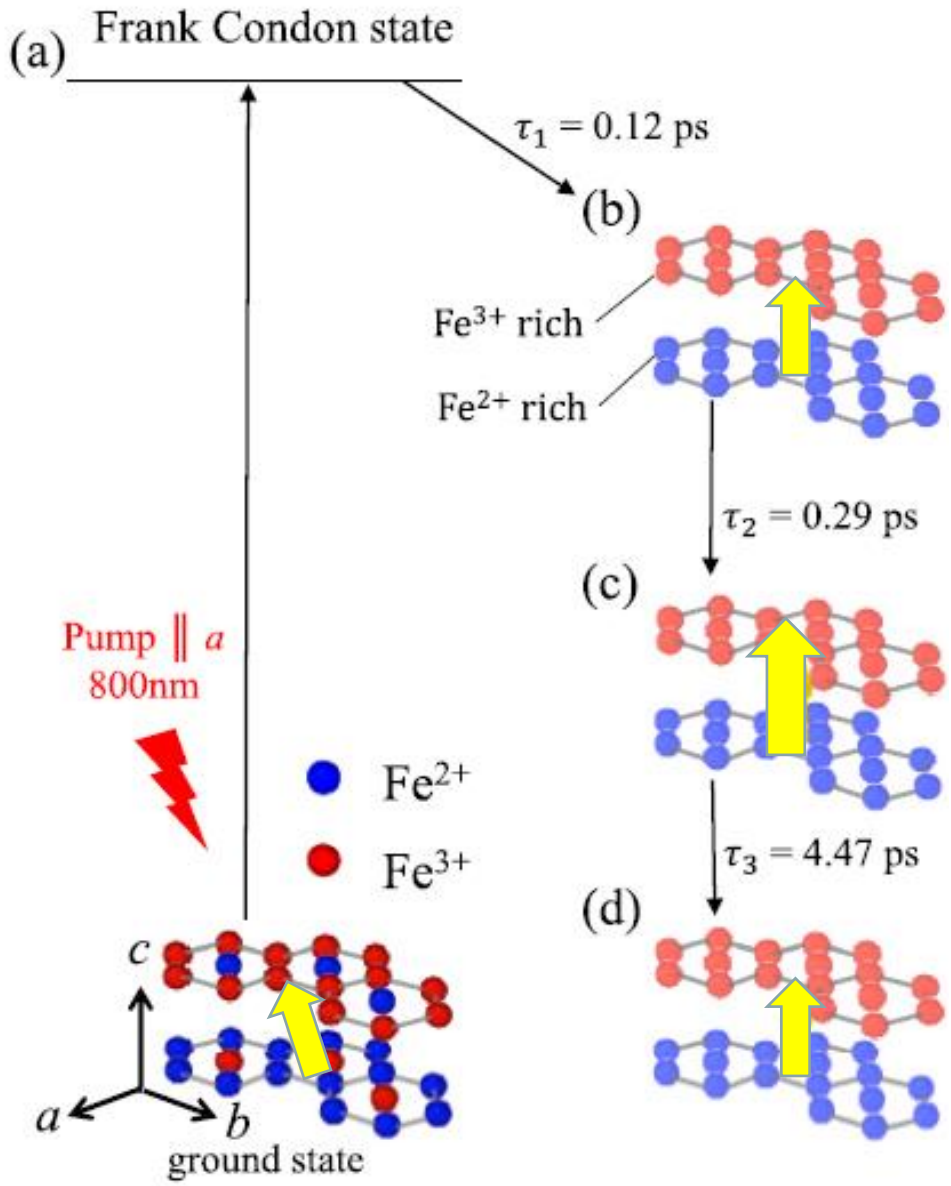
✓ Enhancement of SHG along c-axis!

✓ Tensor components, d_{11}, d_{35}, d_{33} can be evaluated at selected delay times.

→*Enhancement of d_{33}*, indicating an increase of the polarization along the c-axis!

Dynamics of the polarization

$LuFe_2O_4$



1. The charge order in the *W*-layer is largely perturbed, but the charge disproportionation along the c-axis is kept.

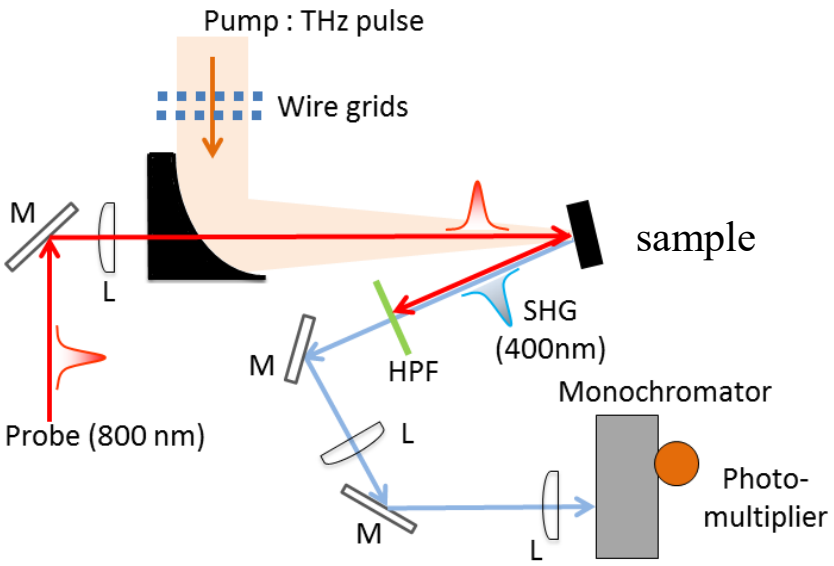
2. Instant enhancement of SHG along the c-axis, keeping the disorder in the ab-plane.
①Photonic change of the lattice constant
② Increase of the correlation length of the disproportionation

3. Long-lived state

Terahertz response

Pump-probe SHG measurement using 100fs terahertz pulse

✓ **Terahertz pulse has locked field oscillation and can be viewed as oscillating strong electric field.**



・TTF-CA (CT complex)
Miyamoto *et al*., Nat. Commun. **4**, 2586 (2013).

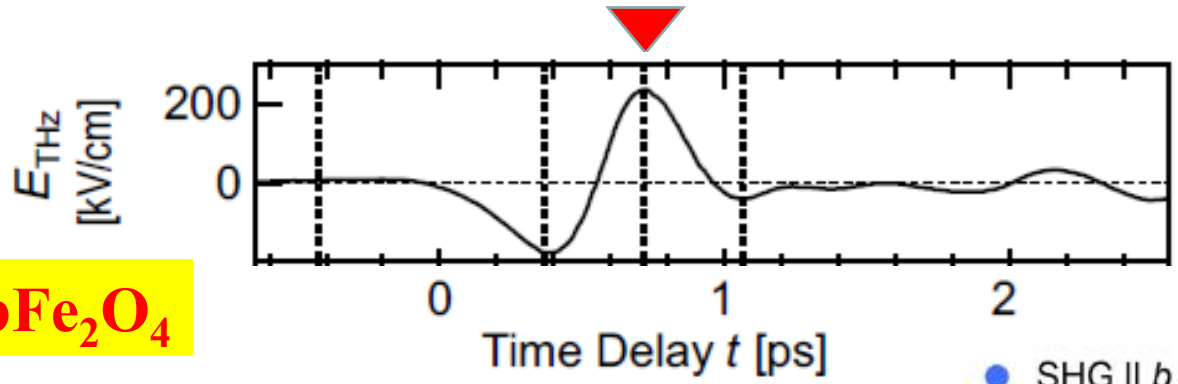
・Oxide perovskites
A. von. Hoegen *et al*., Nature 555, 79 (2018).
Y.O. *et al*., Phys. Rev. Appl. **7**, 064016 (2017).

・Hydrogen bonded FE
Y.O. et al., APL Materials**, 10**, 090702 (2022)
J. Phys. Soc. Jpn. **88**, 013705 (2019), etc….

→Electronic Ferroelectrics?

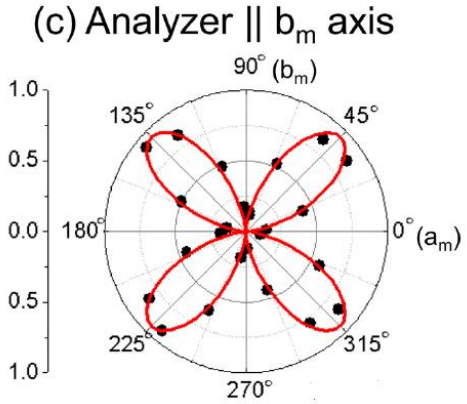
Terahertz response

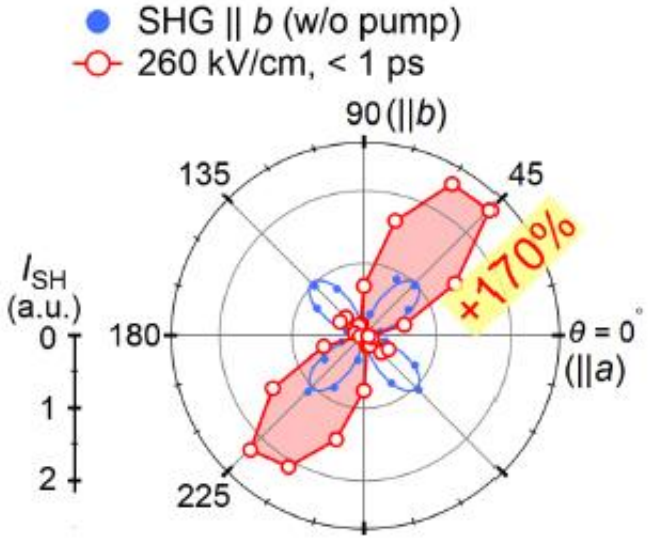
With Iwai G. Tohoku univ.



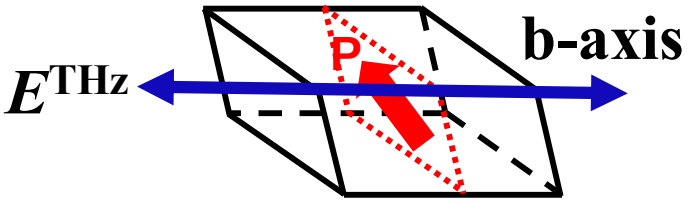
E^{THz} || **b-axis** ($\perp$ **P**)

$YbFe_2O_4$





Cm

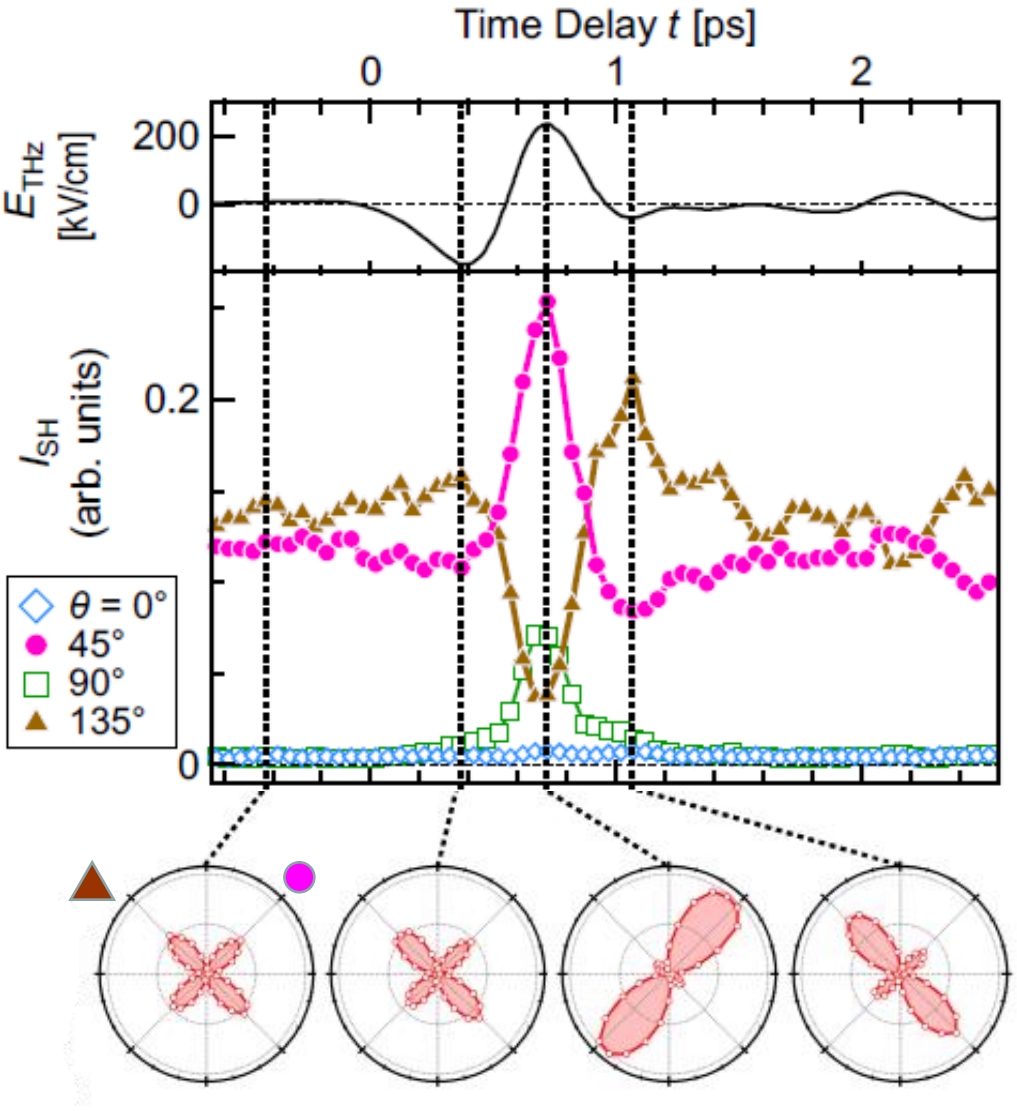


P in *ac*-plane

The applied E^{THz} distorts the monoclinic into a triclinic structure causing the asymmetric change!

Terahertz response

With Iwai G. Tohoku univ.



E^{THz} || b-axis （⊥P）

→The asymmetric change of angle dependence of SHG almost follows the THz waveform.

Ultrafast large change of the direction of P!

Summary

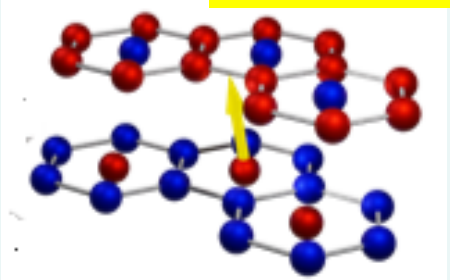
RFe_2O_4 shows Electronic ferroelectricity at room temperature with energy-saving and ultrafast polarization variation.

THz-PHz dynamics

Iwai G.（Tohoku）

Structural dynamics

KEK
SPRING8



Okimoto G.（Tokyo Tech）

SHG and E-M effects

PEEM observation

Okazaki G.（ISSP）

Synthesis

Kataoka G.（AIST）
Ikeda G.（Okayama）

Thermal current

Uchida G.（NIMS）

Thin films and devices

Fujii G.（Okayama）

Memory device

Saitoh G.（Univ. Tokyo）

We intend to strive to replace ordinary ferroelectrics with electronic ferroelectrics.