2-2. IROAST Tenure-track Professor and Associate Professors

No.	Name	Project Title
2-2-1	**Gaochuang CAI**	Design for structural safety and sustainability (DfS3)
2-2-2	**Hiroki MATSUO**	Development of polar materials for energy storage and conversion applications
2-2-3	**Zhongyue ZHANG**	Development of Low Dimensional Magnetism in Metal-Organic Frameworks toward Quantum Informative applications

No. 2-2-1	Design for structural safety and sustainability (DfS3)			
Name	Gaochuang CAI	Title	Associate Professor	
Affiliation	IROAST Email: cai@kumamoto-u.ac.jp			
Research Field	Strengthening resilience / Advanced materials / Data science and AI			

[Details of activities]

1. Research outline and its perspective

Since October 2023, the following main achievements have been archived,

(1) Experimental investigation of seismic performance of highly resilient RC columns

With debonded high-strength steel bars, we have developed innovative RC beam-column joints with high resilience after being subjected to strong earthquakes. The related calculation models are being developed by analyzing the resistance mechanism and failure modes, and a finite element method analysis.

(2) Development of assessment methods of bolted precast RC walls under simulated seismic loads

As a demountable and sustainable structure, a steel-bolted precast RC wall system has been developed and its seismic performance has been experimentally numerically investigated. The construction method of this system is very similar to that of Wall Precast Concrete (PWC) housing in Japan. It has the unique strong and sturdy appearance of reinforced concrete housing and is highly resistant to various disasters. This type of structure is also a form of Design for Deconstruction (DfD) structures, which is of great significance to the sustainable development of future buildings and rapid recovery and reconstruction after disasters.

(3) Development of reinforced CFT columns toward strong earthquake

The seismic behavior of RCFT columns has been experimentally investigated and the design approach of the CFT columns has been proposed including a simplified model for predicting the load-carrying and deformation capacity of the columns.

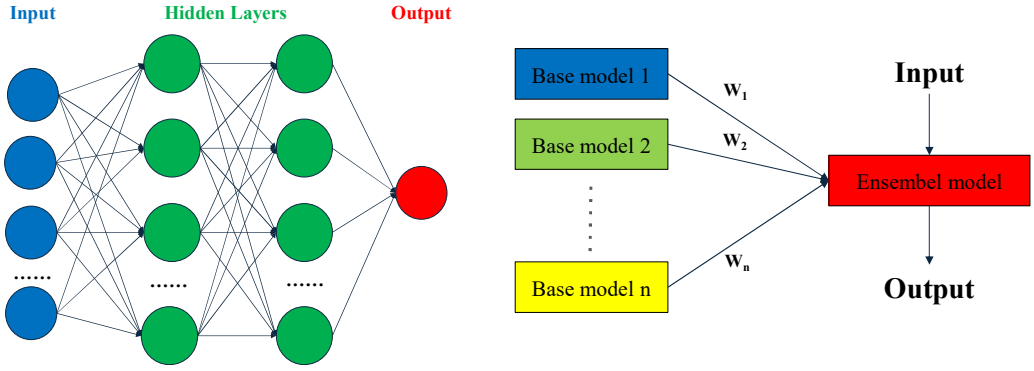
(4) Data-Driven Machine Learning Methods in civil and infrastructures

Reinforced concrete (RC) columns are critical elements in frame structures. A common challenge in structural engineering is estimating the seismic capacity of circular RC columns, as existing methods typically require transforming circular columns into equivalent square sections due to the absence of direct formulas. To address this, this study introduces data-driven machine learning (ML) methods to directly assess both failure modes and seismic shear capacity of circular RC columns.

2. Research progress and results in the fiscal year

As a representative, regarding (4) mentioned in Section 1, with the help of automated machine learning (AutoML), seven ML algorithms were selected and finetuned, resulting in 40 distinct models that were analyzed and compared in detail. The results indicate that the Multilayer Perceptron (MLP) model outperforms others in predicting seismic failure modes, achieving a high accuracy of 88%. For seismic shear capacity predictions, the Weighted Ensemble (WE) model achieved the best performance with Root Mean Squared Error of 53.49, Mean Absolute Error of 39.23, Coefficient of Determination of 0.88 and Mean Squared Error of 2861.18 among all the ML models. Furthermore, the results (the predicted maximum lateral force/the experimental results) of the WE model, with a mean value of 0.98, a standard deviation of 0.11, and a coefficient of variation (mean/standard

deviation) of 12.8%, surpass those of traditional theoretical and empirical models. Besides, the ML models offer fast, accurate seismic performance evaluations for circular RC columns, eliminating the need for complex and time-consuming calculations. Furthermore, SHapley Additive exPlanations (SHAP) analysis provided visual insights into parameter contributions, enhancing model transparency and trust for engineering applications.



(a) MLP (b) Weighted Ensemble (WE)

Fig. 1 Representative algorithms used in the study

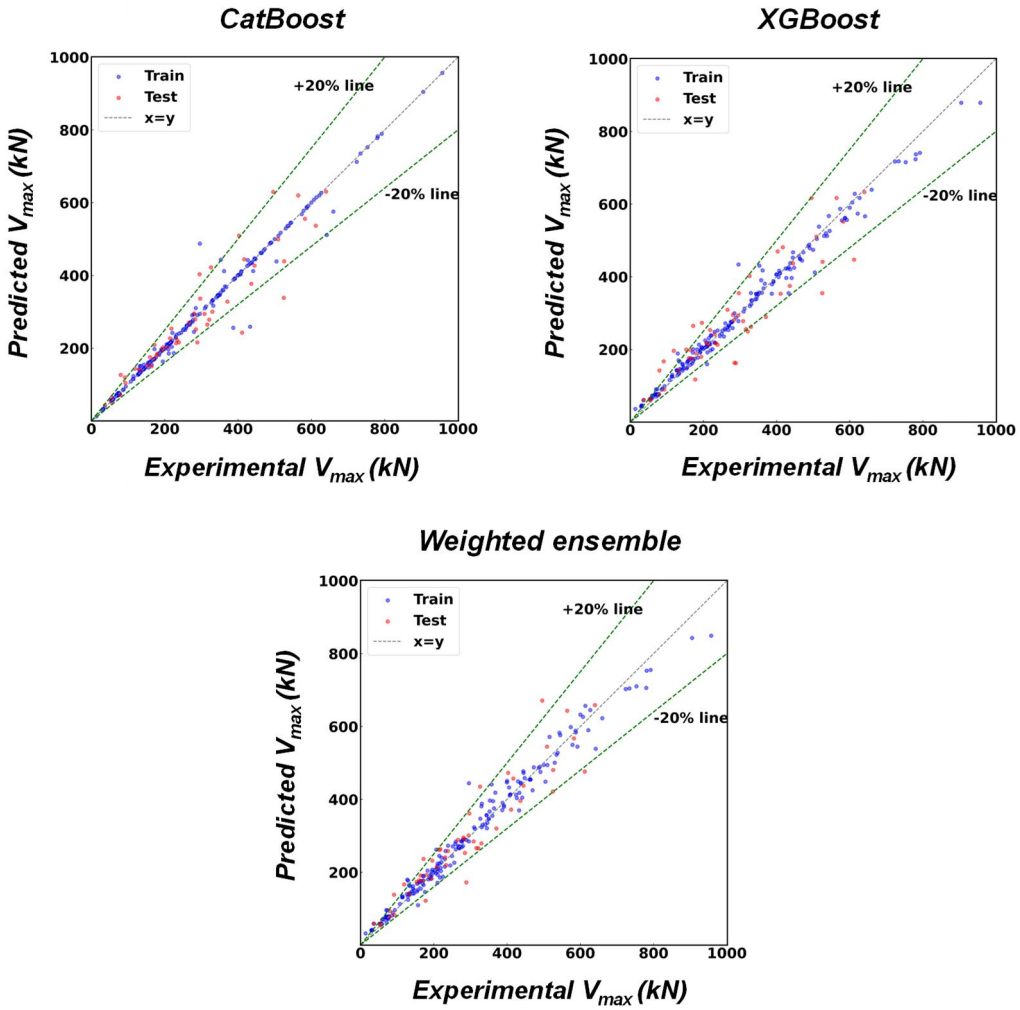


Fig. 2 Comparisons of predicted shear strength and test results

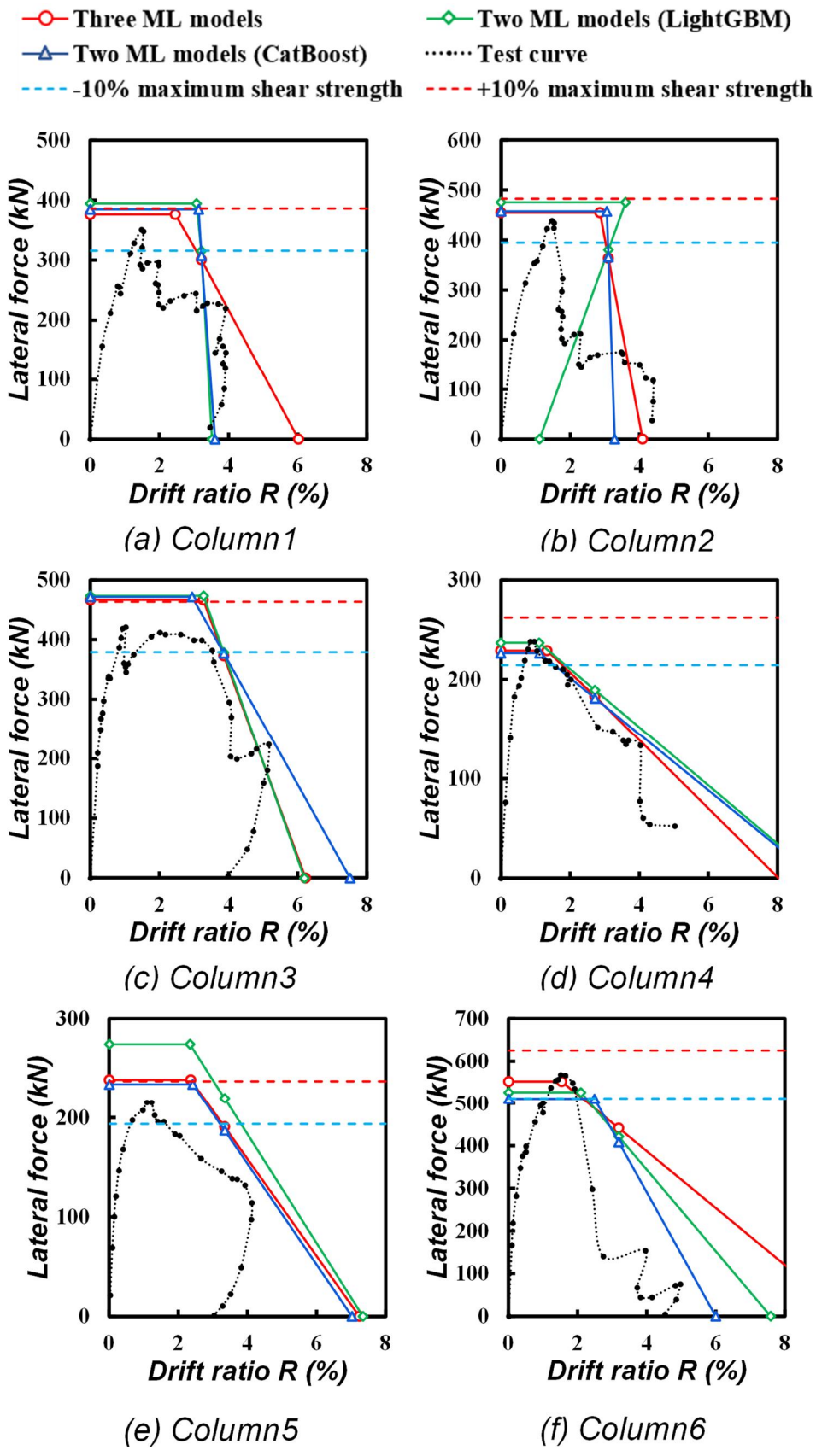


Fig. 3 Validation of ML completed shear strength models

3. Research plan for the next fiscal year

According to the current process and results, the following research projects will be conducted next year.

(1) Seismic performance and FE analysis of Resilient RC(RRC) frames under strong earthquakes
(2) Flexural behavior of steel beam-through CFT joints under cyclic loads
(3) Structural performance and FE analysis of RRC beams under impact loads

4. List of awards, grants, and patents

(1). JSPS科研費基盤研究(B)、レジリエントなPCaRC造柱の開発および性能評価、23K22912、2022-2025、11,830千円、研究分担者
(2). JSPS科研費基盤研究(C)、鋼コンクリート機械的ずれ止めを接合部に用いた新しい中低層CFT構造システムの開発、23K04120、2023-2025、4,680千円、研究分担者

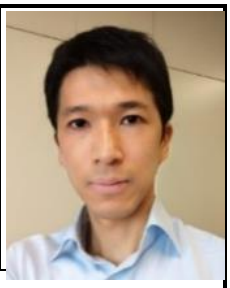
5. List of journal papers in international journal as of the end of December 2024;

1) issued with volume numbers from April 2024 to December 2024

(1). Y. Wen**, **G. Cai***, P. Malla, H. Kikuchi, C. Xie (2024). Seismic Behavior of Resilient Reinforced Concrete Columns with Ultra-High-Strength Rebars Under Strong Earthquake-Induced Multiple Reversed Cyclic Loading, Buildings 2024, 14(12), 3747. **Internship student in IROAST Research Internship Program https://doi.org/10.3390/buildings14123747
(2). Y. Wen**, **G. Cai***, P. Malla (2024). Experimental and Transformer-based Study on Seismic Behavior and Plastic Hinge Length of RC Columns Reinforced with End-Fixed Ultra-high Strength Rebars, Buildings, 2024, 14(10), 3046. **Internship student in IROAST Research Internship Program https://doi.org/10.3390/buildings14103046
(3). J. Zhao, X. Deng**, **G. Cai***, A. Si Larbi***, X. Liu (2024). Shear behavior of reinforced concrete beams with high-strength reinforcements after high temperatures, Construction and Building Materials, 447, 138071 **Internship student in IROAST Research Internship Program *** IROAST Visiting Prof. https://doi.org/10.1016/j.conbuildmat.2024.138071
(4). K. Junaid, N. Algourdin, Z.Mesticou, **G. Cai**, A. Si Larbi*. (2024). The influence of high temperature exposure on the tensile and cracking behavior of crimped-textile reinforced mortar composites (TRMs). Construction and Building Materials, 439, 16, 137350. *IROAST Visiting Prof. https://doi.org/10.1016/j.conbuildmat.2024.137350
(5). K. Junaid, A. Si Larbi*, N. Algourdin, Z.Mesticou, D. Aggelis, **G. Cai.** (2024). Application of supervised learning for classification of cracking and non-cracking major damage in TRMs based on AE features, Construction and Building Materials, 437,137079. *IROAST Visiting Prof. https://doi.org/10.1016/j.conbuildmat.2024.137079.
(6). **G.Cai***, Y. Wen**, Malla Prafulla, Takashi Fujinaga and Amir Si Larbi*** (2024). Effect of axial load and shear span on seismic performance of CFT columns reinforced with end-fixed ultra-high strength rebars. Bull Earthquake Eng, 22(9), 4515-4543, 2024. **Internship student in IROAST Research Internship Program *** IROAST Visiting Prof. https://doi.org/10.1007/s10518-024-01939-4
(7). Jun Zhao, Yibo Jiang, **Gaochuang Cai**, Xiangsheng Deng*, Amir Si Larbi** (2024). Flexural stiffness of RC beams with high-strength steel bars after exposure to elevated temperatures. Structural Concrete, 25(5), 3081-3102. *Internship student in IROAST Research Internship Program ** IROAST Visiting Prof. https://doi.org/10.1002/suco.202300934

2) scheduled to be issued with volume numbers from January 2025 to March 2025 and confirmed to be issued thereafter as of the end of December

(1). Yue Wen#, Shiqiao Zhou#, **G. Cai***, Zhili He, Amir Si Larbi. Comprehensive Assessment of Failure Mode and Shear Capacity of Reinforced Concrete Circular Columns Based on Data-Driven Machine Learning Methods, Engineering Applications of Artificial Intelligence.2025

No. 2-2-2	Development of polar materials for energy storage and conversion applications			
Name	Hiroki MATSUO	Title	Associate Professor	
Affiliation	IROAST Email: matsuo_h@cs.kumamoto-u.ac.jp			
Research Field	Advanced materials			

[Details of activities]

1. Research outline and its perspective

We have developed ferroelectric materials with defect dipoles and relaxor ferroelectrics for the application to multi-layered ceramic capacitors (MLCCs) with a high energy density. The ferroelectric and dielectric properties of ceramics of Cu/Fe-doped $BaTiO_3$, La-doped $BaTiO_3$–$Bi(Zn_{2/3}Ta_{1/3})O_3$ (BLT–BZT) (Fig. 1), and $(Bi_{1/2}K_{1/2})TiO_3$-$(Bi_{1/2}Li_{1/2})TiO_3$ (BKT–BLT) were investigated. Moreover, the bulk photovoltaic properties of Cu-doped $LiNbO_3$ ferroelectric single crystals were investigated, and novel lead-free hybrid organic-inorganic perovskite was synthesized for the development of visible-light active narrow-gap ferroelectrics.

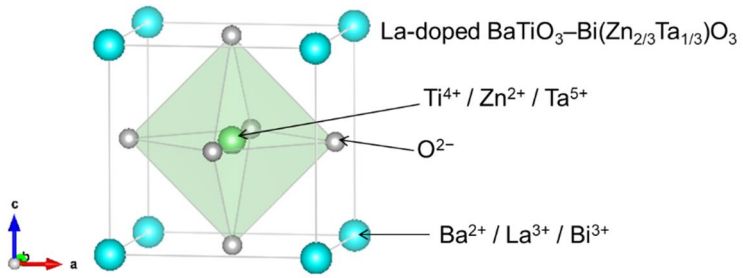


Fig. 1. Crystal structures of perovskite-type La-doped $BaTiO_3$–$Bi(Zn_{2/3}Ta_{1/3})O_3$ solid solutions.

2. Research progress and results

a. Ferroelectric $BaTiO_3$ has been widely used as a dielectric material for MLCCs because of its high dielectric permittivity. In transition metal-doped $BaTiO_3$, it has been proposed that acceptors on the Ti site trap oxygen vacancies ($V_O^{\bullet\bullet}$) to form defect dipoles [Fig. 2(a)]. We investigate the electrical properties of Cu-doped and Fe-doped $BaTiO_3$ ceramics with defect dipoles to reveal the differences in the polarization properties and the formation process of defect dipoles. The ceramics annealed at higher temperatures show typical single polarization (P)-electric field (E) hysteresis loops [Fig. 2(b)] while ceramics annealed at lower temperatures exhibit pinched P-E loops with higher energy density (U_{rec}) due to the presence of defect dipoles [Fig. 2(c)]. The annealing temperature dependence of remanent polarization suggests that Fe-doped $BaTiO_3$ exhibits higher temperature stability than Cu-doped $BaTiO_3$ probably because of the higher $V_O^{\bullet\bullet}$ trapping energy of Fe than Cu. I received the Kumamoto University Research Achievement Award for accomplishments related to this research on defect dipoles.

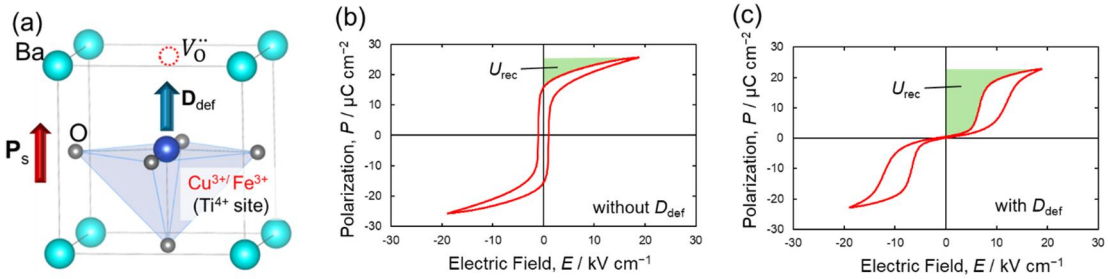


Fig. 2(a) Schematic crystal structure of Cu/Fe-doped $BaTiO_3$ around an acceptor atom. Polarization properties of Cu-doped $BaTiO_3$ ceramics (b) without and (c) with defect dipoles (D_{def}).

b. Relaxor ferroelectrics are promising materials for energy storage ceramic capacitors because of their high recoverable energy density and high energy efficiency. We develop ceramics of $BaTiO_3$-based relaxor ferroelectrics of BLT–BZT for MLCC applications in collaboration research with Dr. G. A. Babu from SSN College of Engineering. The BLT–BZT ceramics showed the temperature of maximum relative permittivity lower than room temperature while undoped $BaTiO_3$ has a Curie temperature of around 120 °C. For the BLT–BZT solid solutions, a deviation from the Curie-Weiss law was observed in the temperature dependence of the dielectric constant, demonstrating the formation of polar nanoregions characteristic of relaxor ferroelectrics. Slim *P-E* loops with a suppressed remanent polarization were observed for the solid solution ceramics, and a recoverable energy density of 1.46 J/cm³ at 200 kV/cm was achieved, along with an ultrahigh energy storage efficiency of 92.8 %.

Moreover, relaxor behavior and energy storage properties of BKT–BLT relaxor ferroelectric ceramics were analyzed with the cooperation of Prof. Z. G. Ye from Simon Fraser University. It was suggested that the substitution of Li for K stabilizes the relaxor phase by introducing a structural disorder in the BKT matrix.

c. The bulk photovoltaic effect in undoped and Cu-doped $LiNbO_3$ single crystals was investigated. Our Cu-doped single crystals exhibited larger bulk photovoltaic elements (β_{33} and β_{31}) than previously reported values because of the optimal redox state of Cu and higher Cu content [Fig. 3(a)]. The Cu-$LiNbO_3$ single crystals annealed at an optimal reducing atmosphere exhibited a quite high open-circuit voltage of 1700 V under simulated sunlight whereas the photoresponse of the undoped crystals was negligibly small. These results demonstrate that gap states derived from Cu-3d orbitals act as an active center for carrier generation under below-bandgap excitation [Fig. 3(b)] and promote the bulk photovoltaic effect. Moreover, we have started the development of novel ferroelectric hybrid organic-inorganic perovskites (HOIP) having smaller bandgap energy than conventional ferroelectric oxides. The successful synthesis of lead-free HOIPs with a layered crystal structure was suggested by the X-ray diffraction measurements for powder samples prepared by the re-precipitation method.

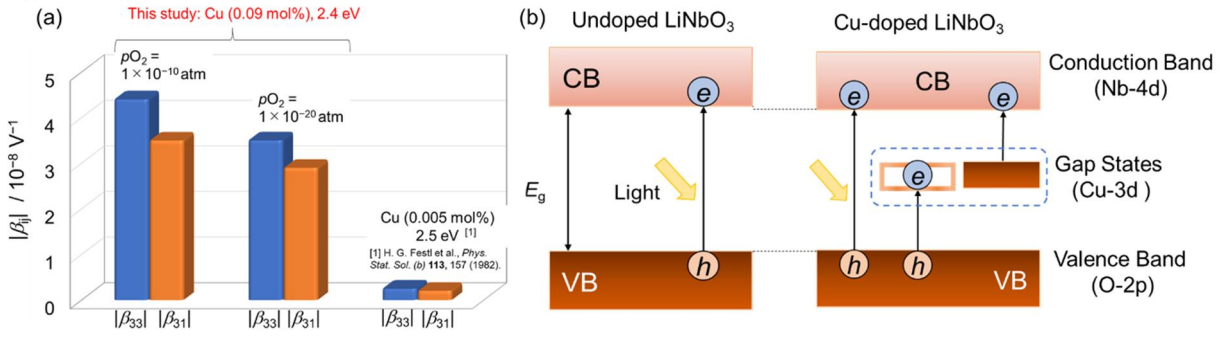


Fig. 3(a) Bulk photovoltaic tensor elements of Cu-doped $LiNbO_3$ single crystals. (b) Schematic band diagrams of undoped and Cu-doped $LiNbO_3$.

3. Research plan for the next year

a. To evaluate the stability of defect dipoles under electric fields, the electrical fatigue properties of *P-E* loops of Cu/Fe-doped $BaTiO_3$ ceramics with defect dipoles will be measured. This measurement will clarify the mobility of $V_O^{\bullet\bullet}$ trapped by acceptors and provide important information for practical applications.

b. To obtain higher energy density, further improvement of breakdown field and maximum polarization will be tried by developing Bi-based relaxor ferroelectrics.

c. The growth of single crystals of the lead-free HOIPs will be conducted to determine their precise crystal structures. Moreover, epitaxial thin films will be also prepared by the mist-CVD method for the ferroelectric and photovoltaic measurements.

4. List of Papers

1) Hiroki Matsuo*, Tomoki Sato, and Yuji Noguchi*
"Bulk photovoltaic effect in Cu-doped $LiNbO_3$ single crystals with controlled oxidation state"
Japanese Journal of Applied Physics 63, 07SP08 (2024).
https://iopscience.iop.org/article/10.35848/1347-4065/ad60cf

2) Hiroki Matsuo* and Yuji Noguchi*
"Bulk photovoltaic effect in ferroelectrics"
Japanese Journal of Applied Physics 63, 060101 (2024). (**Invited Review**)
https://iopscience.iop.org/article/10.35848/1347-4065/ad442e

5. List of Awards and Grants

(Award)

1) Kumamoto University Research Achievement Award FY2024
"Utilizing ferrorestorable polarization in energy-storage ceramic capacitors" November 2024

Fig. 4. Photograph of Kumamoto University Research Achievement Award ceremony

2) The 8th International Workshop on Relaxor Ferroelectrics (IWRF 2024) Best Poster Award
Kotaro Saito, Hiroki Matsuo, Yuji Noguchi* (Kumamoto Univ.), Hiroshi Nakajima, Shigeo Mori (Osaka Metropolitan Univ.), Zuo-Guang Ye (Simon Fraser Univ.)
"Relaxor behavior and energy storage properties of $(Bi_{1/2}K_{1/2})TiO_3$-$(Bi_{1/2}Li_{1/2})TiO_3$ solid solution ceramics" October 28th, 2024, Xi'an (China)

(Grants)

1) JSPS KAKENHI Grant-in-Aid for Transformative Research Areas (A)
"Control of Defect Dipoles for Designing Hyper-Ordered Structure in Ferroelectric Perovskite Oxides", April 2023-March 2025.
2) Murata Science and Education Foundation
"Development of organic-inorganic hybrid ferroelectric thin films exhibiting the bulk photovoltaic effect under visible light illumination", September 2024–August 2025.

No. 2-2-3	Development of Low Dimensional Magnetism in Metal-Organic Frameworks toward Quantum Informative applications			
Name	Zhongyue ZHANG	Title	Associate Professor	
Affiliation	IROAST Email: zhongyuezhang@kumamoto-u.ac.jp			
Research Field	Advanced materials			

[Details of activities]

1. Research outline

Low dimensional magnetism is considered as one of the most intriguing and challenging fields in traditional solid-state physics, however, the precise control of dimensionality is always a challenge. In our research, low dimensional magnetism will be pursued via rational design of metal-organic frameworks, including 2D magnetism toward Kitaev spin liquid, 1D magnetism toward spintronic devices and 0D magnetism toward artificial NV centers for quantum sensing.

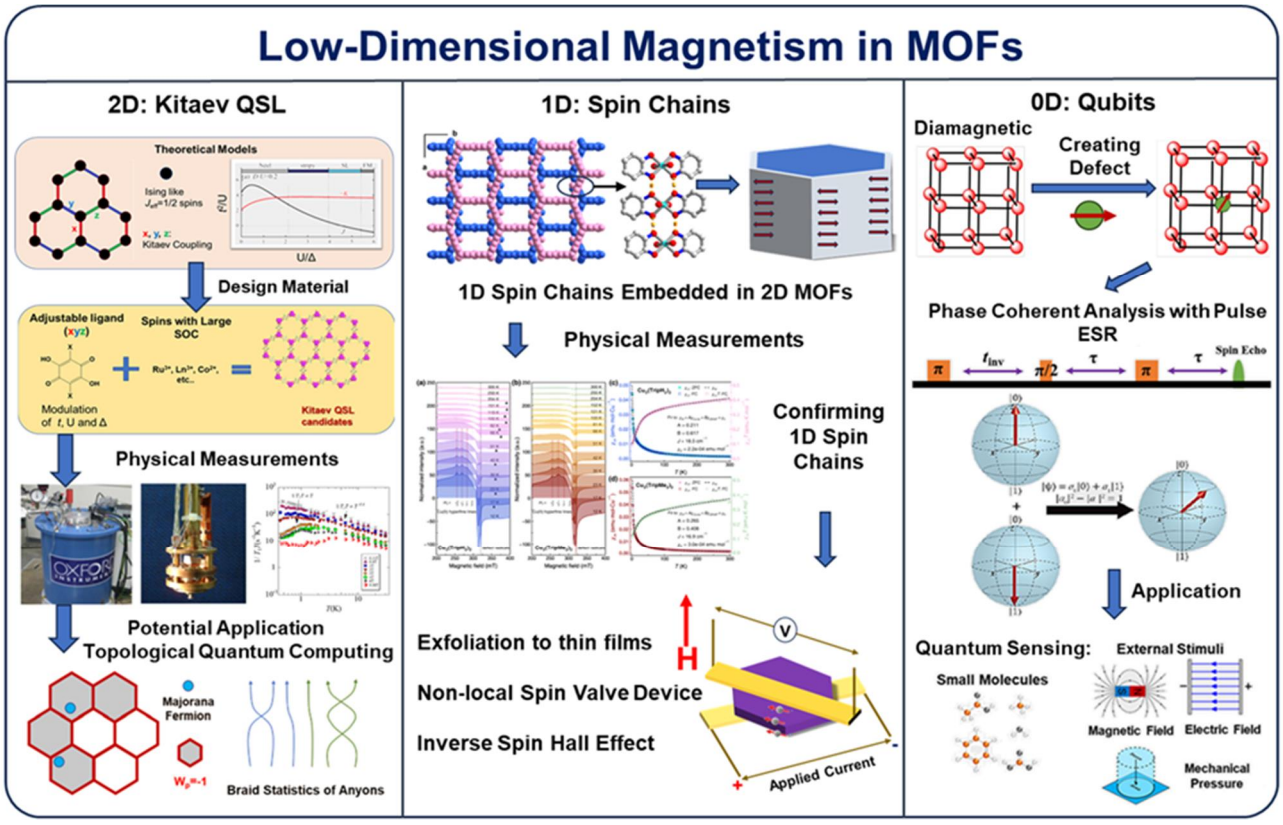


Fig.1 Conceptual scheme of research outline

2. Research progress and results in the fiscal year

1D magnetism: for formerly prepared 2D MOFs, $Cu_3(TripH_2)_2$ and $Cu_3(TripMe_2)_2$, we have performed careful CW-ESR and magnetism studies, as well as single crystal conductivity measurements. From the ESR study, we observed both significantly broadened peaks, the peak width of which narrowed upon the decrease of measurement temperatures. Meanwhile, magnetic susceptibility measurement and magnetization measurements both indicated susceptibility and magnetization that were far lower than

the paramagnetic assumption, suggesting a strong antiferromagnetism existing in these MOFs. Although single crystal conductivity measurements suggest that these MOFs are poor semiconductors with in-plane conductivity being ~2×10^{-7} S/cm and 0.3×10^{-7} S/cm, as these MOFs were able to be exfoliated into thin films, they are still promising materials as the spin-filtering active layer in spintronic devices.

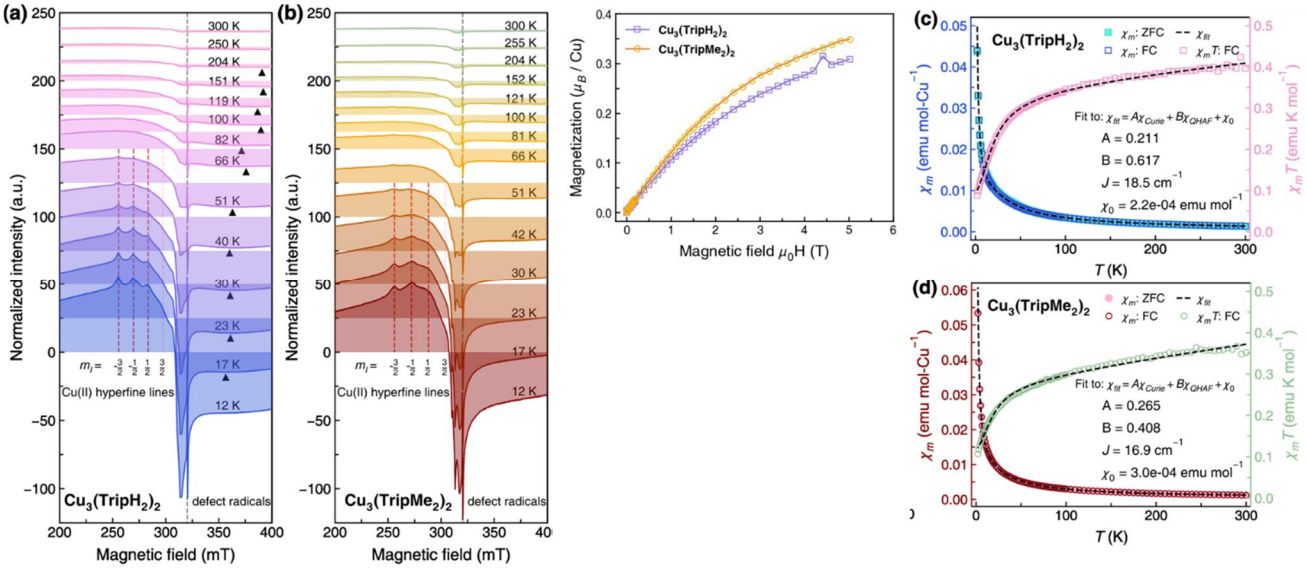


Fig.2 ESR and magnetism showing the 1D AFM behavior in these MOFs.

2D magnetism: We are continuing the physical measurements on Kitaev spin liquid candidate, $Ce_2(ox)_3(H_2O)_6\cdot4H_2O$. By performing the magnetic field dependent heat capacity measurement with the applied field direction along the *b* axis (out-of-plane) and *a* axis(inplane), a clear difference is observed that with applied field in *b* direction, the heat capacity of Ce^{3+} exhibited a Schottky-like behavior with a linear C/T-T component at ultralow temperature, which was rational for these J_{eff} = 1/2 pseudo spins with strong anisotropy. However, with the field is applied along *a* axis, no linear C/T-T component could be observed, and the energy gap is found to be proportional to the applied magnetic field, which may hint

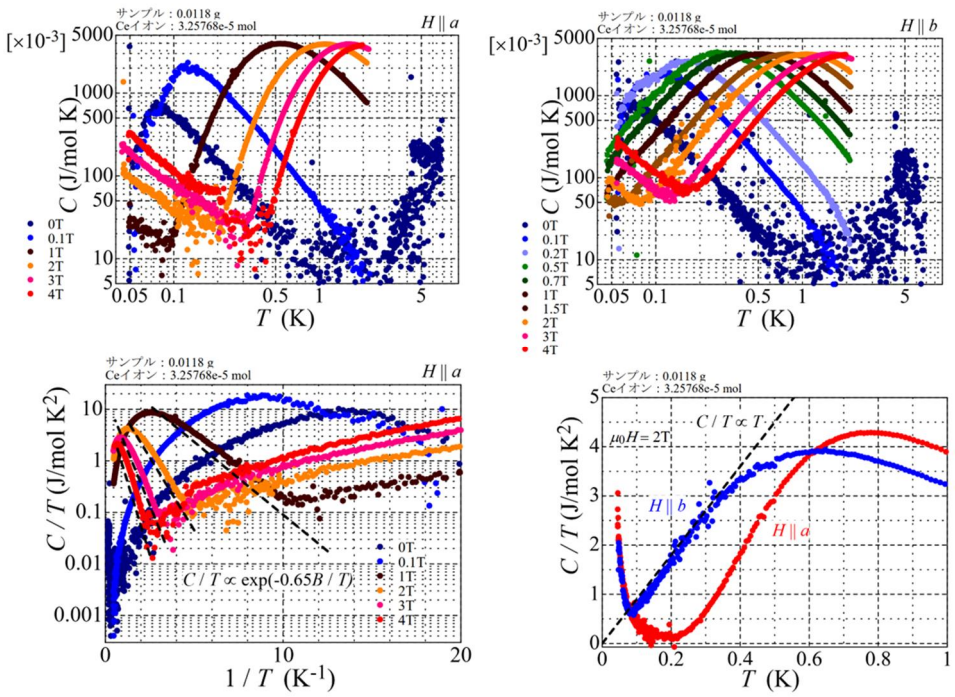


Fig.3 Field-dependent heat capacity of $Ce_2(ox)_3(H_2O)_6\cdot4H_2O$

a so-called Majorana gap predicted by the theory of Kitaev spin liquid. Therefore, there was a high chance that $Ce_2(ox)_3(H_2O)_6{\cdot}4H_2O$ was the first MOF-based Kitaev spin liquid, which was simply predicted by the crystal engineering approach.

0D magnetism: Since we managed to grow gigantic single crystals of $Ln_2(ox)_3(H_2O)_6{\cdot}4H_2O$ (Ln=La-Gd) and this crystal system contains only oxalate ligands and water molecules, therefore, by deuteration, it is possible to create a nuclear spin free environment, which may significantly elongate the coherence time. By doping paramagnetic ions, such as Ce^{3+} into diamagnetic $La_2(ox)_3(H_2O)_6{\cdot}4H_2O$, a spin-qubit doped single crystal could be achieved. By stepwise deuteration, both the relaxation time (T_1) and coherence time (T_2) could be tuned, which lead to a quantum sensing system for D_2O/H_2O.
As a result, we prepared single crystals of $La_2(ox)_3(H_2O)_6{\cdot}4H_2O$ with a doping of 0.5%Ce(III), and subjected to pulse ESR analysis. Angle dependent echo-detected field sweep analysis (EDFS) of single crystals exhibited periodic feature with the rotation angle, and surprisingly, at least 2 types absorption could be observed, which is contradict to the fact that only one crystallographic independent Ce(III) exists in the crystal structure. Furthermore, deuteration was performed by heating these crystals in D_2O and echo-detected ESR measurements were applied to measure T1 and T2 for as-prepared crystals and deuterated crystals. At low temperature like 3.5K, intrinsic Ce(III) doped MOF exhibits a T2 of 4.5μs, and after the deuteration, this coherence time was elongated to 7.4μs and the decay upon the increase of temperature was also suppressed. These results suggest deuteration is an effective strategy for manipulating both the relaxation and coherence time of spin qubits doped in MOFs.

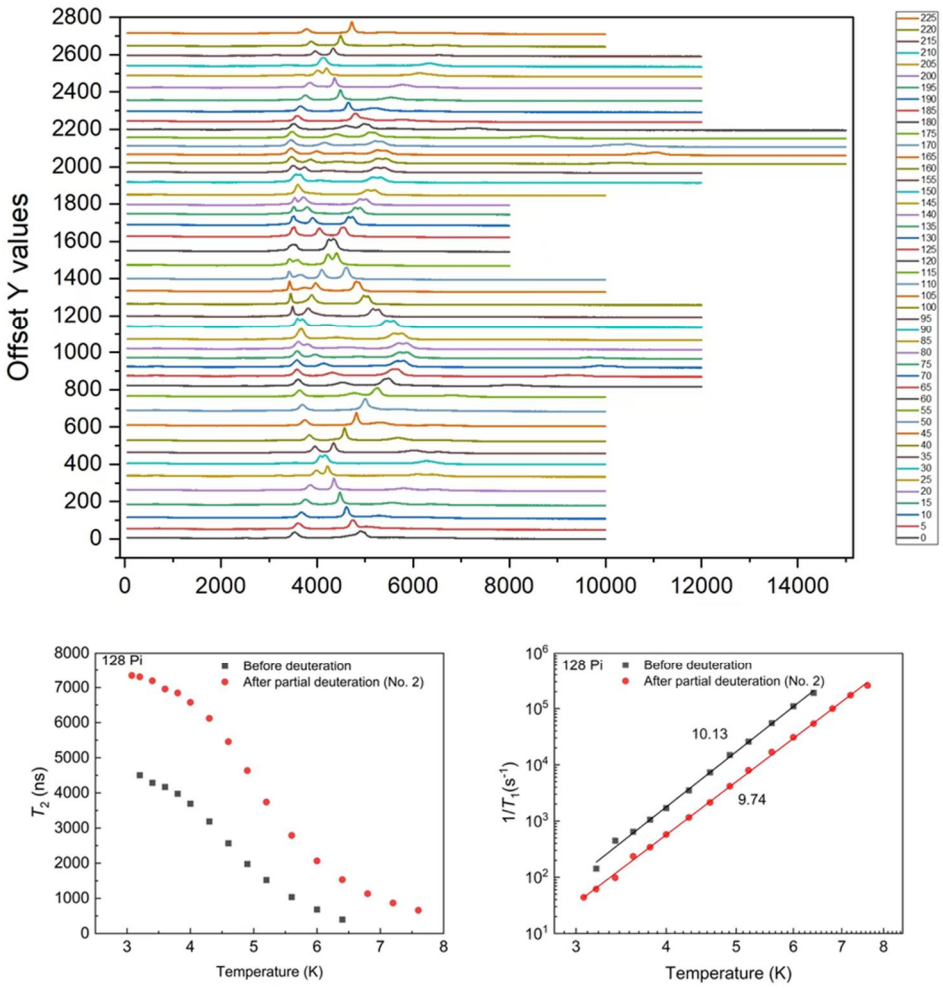


Fig.4 Angle-dependent EDFS and echo-detected EPR measurements.

3. Research plan for the next fiscal year

1D magnetism: The research has been completed and submitted to *J. Am. Chem. Soc.*, currently the manuscript is being revised, the publication will be finished within the next fiscal year.
2D magnetism: More single crystals will be synthesized and ones with better morphologies will be picked for single crystal measurements. With better crystals, more detailed in-plane measurements will be conducted to investigate the angular dependent in-plane heat capacity and compared with theoretical predicted ones.
0D magnetism: Stepwise deuteration will be performed on Ce(III)-doped $La_2(ox)_3(H_2O)_6 \cdot 4H_2O$ crystals and pulse ESR measurements will be further conducted on these crystals. The mechanism will be analyzed by incorporating with single crystal structure analysis and theoretical calculations.
Chirality in 2D conductive MOFs: We will design and prepare a series of truxene-derivative based ligands with specific chirality and synthesize new chiral 2D conductive MOFs with these ligands. The relationship between chirality and spin-selective transport properties of these MOFs will be investigated to study CISS effects.

4. List of publications.

1. Solvation/desolvation induced reversible distortion change and switching between spin crossover and single molecular magnet behaviour in a cobalt(ii) complex.
   H. Zenno, Y. Sekine, Z. Zhang and S. Hayami, *Dalton Trans.*, **2024**, *53*, 5861-5870.
2. Assembling Smallest Prussian Blue Analogs Using Chiral Hydrogen Bond-Donating Unit toward Complete Phase Transition. R. Fukushima, Y. Sekine*, Z. Zhang, Shinya Hayami*, *J. Am. Chem. Soc.*, **2024**, *146*, 24238–24243.
3. Purification and tailored functionalities in detonation nanodiamond
   L. I. Ardhayanti, Md. S. Islam, C. Ze, M. Fukuzaki, X. Liu, Z. Zhang, Y. Sekine, S. Hayami, *Bull. Chem. Soc. Jpn.*, **2024**, *97*, uoae089