

2019年度第1回シンクロトロン光産業利用セミナー
愛知県産業労働センター「ウイंकあいち」
2019.09.30

粉体材料における放射光実験の高速化に向けて - マテリアルズインフォマティクスへ繋げるために -

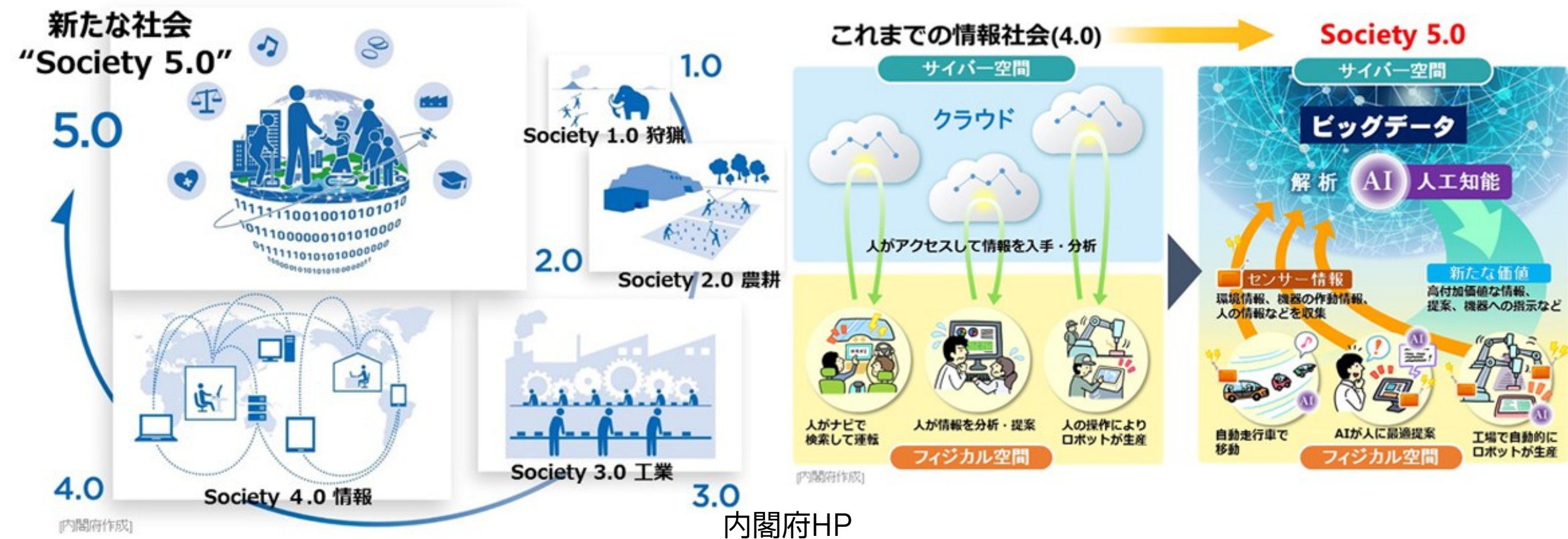
藤本 憲次郎

(東京理科大学 理工学部 先端化学科)



材料探索技術 “Society 5.0に対応した材料研究”

- コンビナトリアル技術
- マテリアルズインフォマティクス (AIや機械学習)



- 狩猟社会 (Society 1.0)
- 農耕社会 (Society 2.0)
- 工業社会 (Society 3.0)
- 情報社会 (Society 4.0)

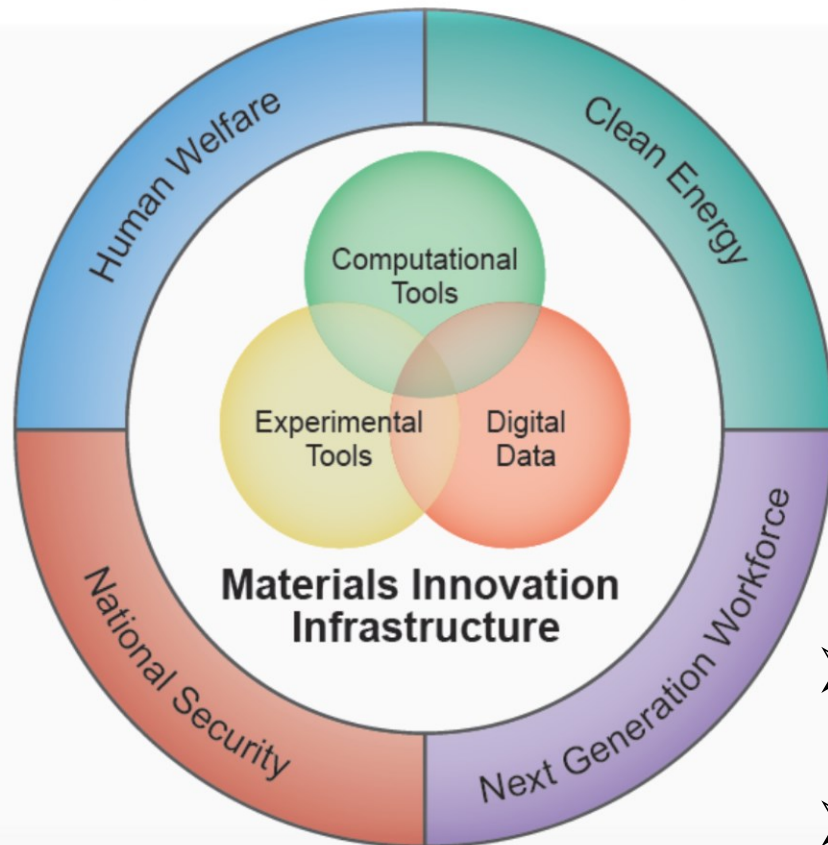
サイバー空間 (仮想空間) とフィジカル空間 (現実空間) を高度に融合させたシステムにより、経済発展と社会的課題の解決を両立する、人間中心の社会 (Society)

Materials Genome Initiative (MGI)

マテリアルズ ゲノム イニシアチブ

Materials Genome Initiative
for Global Competitiveness

June 2011



マテリアルイノベーションには

- Computational tools

- ✓ DFT calculation
- ✓ First principle
- ✓ Machine learning

- Digital data

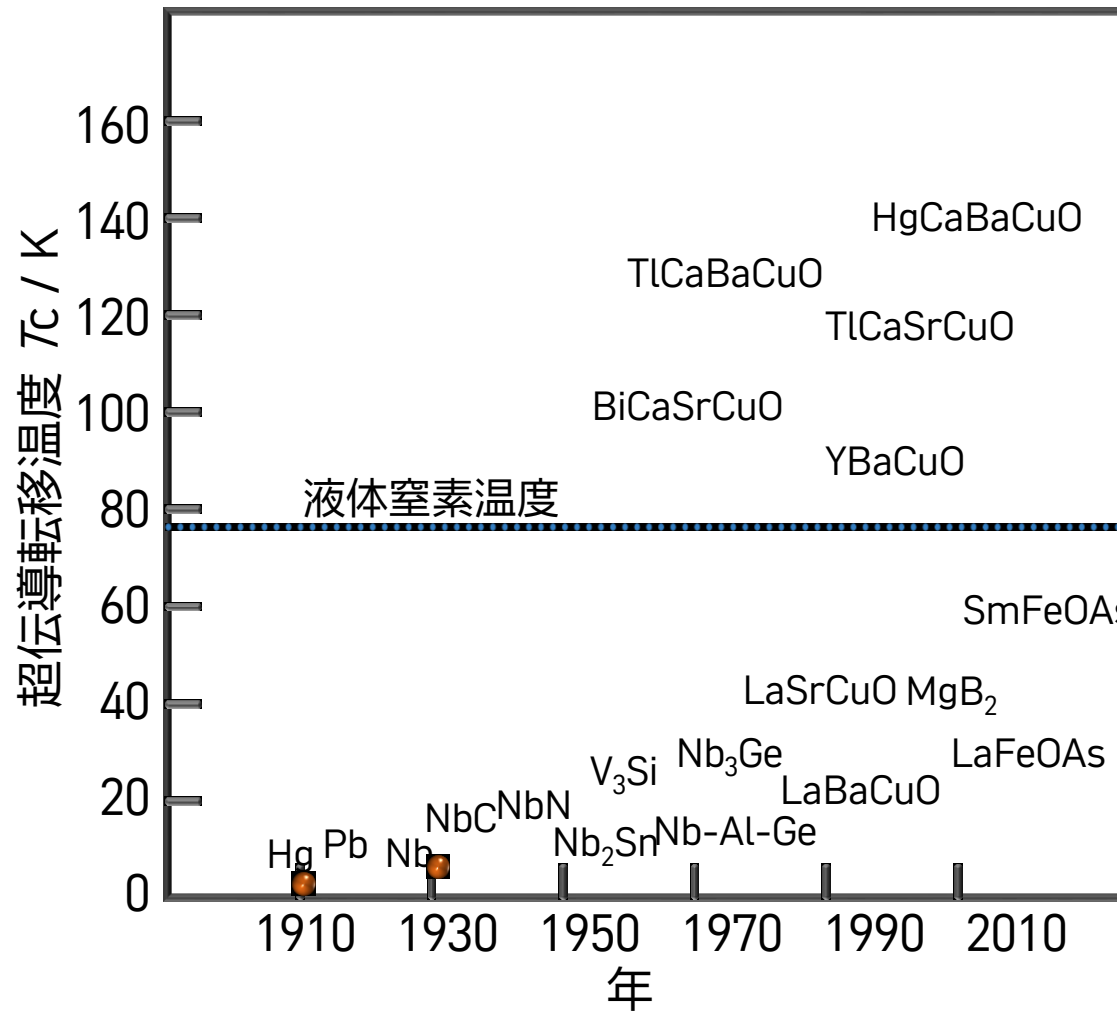
- ✓ Text data mining of physical and/or chemical property

- Experimental tools

- ✓ Combinatorial HT technology

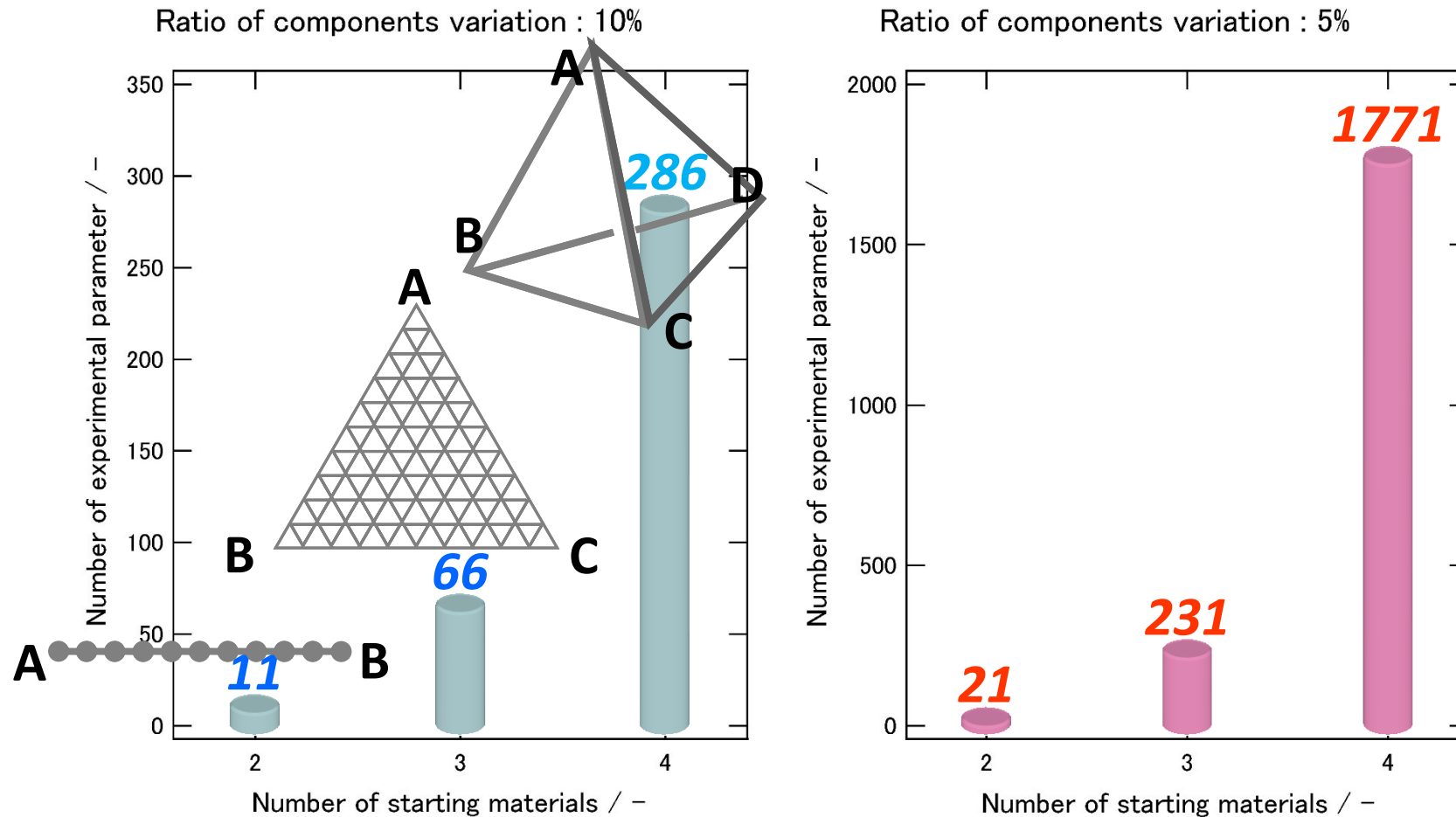
- 近年の発表では Computational tools と Digital data による材料探索が大半
- 精度の高い材料探索を進めるには三つ巴が大事

原料成分多次元化の推移 (例：超伝導材料)



超伝導材料に限らず、多くの機能材料で発見される新素材は年を追うごとに多成分系から構成されている

多成分系の材料探索における問題点



対象となる成分(横軸)が増えるほど、
実験パラメータ(縦軸: 実験に必要な条件)は指数関数的に増大

COMBINATORIAL CHEMISTRY

Progress in dynamic combinatorial chemistry, polymer-supported reagents, microwave heating, functional studies, and deconvolution advance the field

STU BORMAN, C&EN WASHINGTON

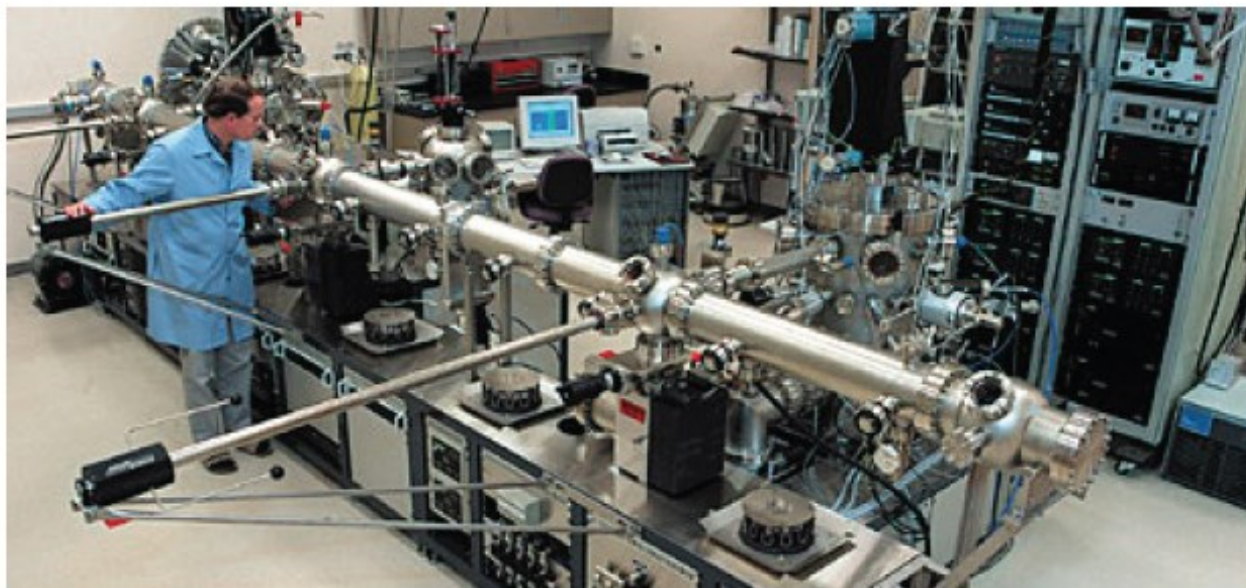


MANY AT A TIME Program head Andreas Marzinik (front to back) and lab specialists Raphael Gattlen and Urs Rindisbacher of Novartis Pharma AG, Basel, Switzerland, pipette coupling reagent into 96-well reaction blocks.

INORGANICS GO COMBINATORIAL

Combinatorial synthesis is leading to new alloys, catalysts, and magnetic semiconductors

RON DAGANI, C&EN WASHINGTON



HIGH-TECH FILMS This molecular beam epitaxy system at Pacific Northwest National Laboratory was used to grow high-quality films of a room-temperature magnetic semiconductor discovered by a Japanese team using the combinatorial approach.

PACIFIC NORTHWEST NATIONAL LABORATORY

コンビナトリアルテクノロジーが産まれるきっかけ

Combinatorial chemistry

Solid-phase peptide synthesis (固相ペプチド合成)

R.B. Merrifield,

J. Am. Chem. Soc. **85**, 1963, 2149–2154

[CONTRIBUTION FROM THE ROCKEFELLER INSTITUTE, NEW YORK 21, N. Y.]

Solid Phase Peptide Synthesis. I. The Synthesis of a Tetrapeptide¹

BY R. B. MERRIFIELD

RECEIVED JANUARY 31, 1963

A new approach to the chemical synthesis of polypeptides was investigated. It involved the stepwise addition of protected amino acids to a growing peptide chain which was bound by a covalent bond to a solid resin particle. This provided a procedure whereby reagents and by-products were removed by filtration, and the recrystallization of intermediates was eliminated. The advantages of the new method were speed and simplicity of operation. The feasibility of the idea was demonstrated by the synthesis of the model tetrapeptide L-leucyl-L-alanylglycyl-L-valine. The peptide was identical with a sample prepared by the standard *p*-nitrophenyl ester procedure.

- ✓ Merrifield は一回の実験で様々なペプチドを合成する効率的な手法を提案。これにより1984年にノーベル化学賞を受賞。
- ✓ この概念は医薬・創薬業界で広く利用されている。

コンビナトリアルケミストリーを提案したのは Merrifield博士だけではなかった・・・？

- ✓ K. Kennedy, T. Stefansky, G. Davy, V.F. Zackay and E.R. Parker,
**Determination of a ternary-alloy phase diagram using
e-beam co-evaporation**, *Journal of Applied Physics* **36**, 3808 (1965).
- ✓ Miller *et al.*,
Au-SiO₂ composition spread fabricated by co-sputtering,
APL **10**, 86 (1967).
- ✓ Hanak, J.J.
“Multiple-sample concept,”
Journal of Materials Science **5**, 964 (1970).

1960年代に3名の研究チームが無機化学・金属の分野で挑戦

なぜ発展しなかった？

- ✓ 研究を効率化するツール(パソコン・高速評価装置など)がなかった

無機系コンビナトリアルテクノロジーの発達

1990's ~

- ✓ Discovery of high T_c superconductivity led to development of automated high throughput synthesis techniques.

A Combinatorial Approach to Materials Discovery

X.-D. Xiang,* Xiaodong Sun, Gabriel Briceño, Yulin Lou, Kai-An Wang, Hauyee Chang, William G. Wallace-Freedman, Sung-Wei Chen, Peter G. Schultz*

A method that combines thin film deposition and physical masking techniques has been used for the parallel synthesis of spatially addressable libraries of solid-state materials. Arrays containing different combinations, stoichiometries, and deposition sequences of BaCO_3 , Bi_2O_3 , CaO , CuO , PbO , SrCO_3 , and Y_2O_3 were generated with a series of binary masks. The arrays were sintered and BiSrCaCuO and YBaCuO superconducting films were identified. Samples as small as 200 micrometers by 200 micrometers in size

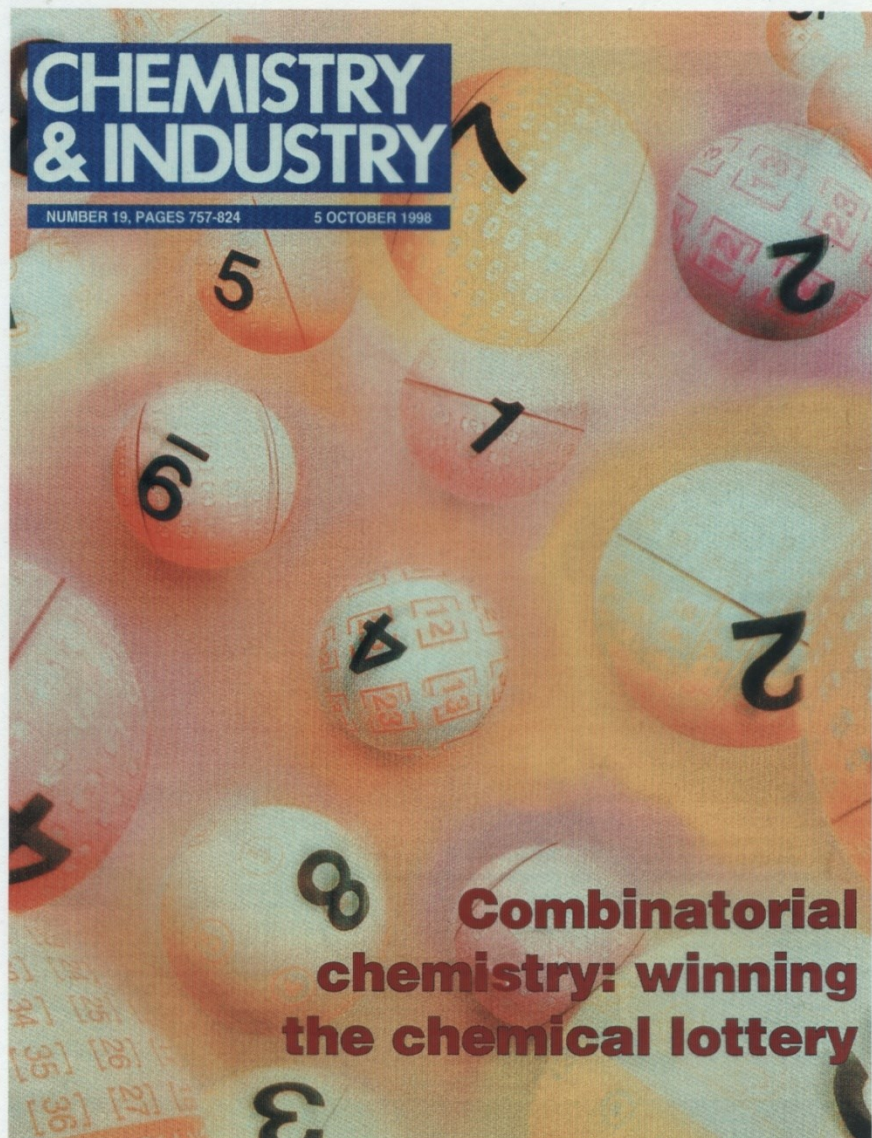
A method that combines thin film deposition and physical masking techniques has been used for the parallel synthesis of spatially addressable libraries of solid-state materials.



Science 268, 1738 (95)

CHEMISTRY & INDUSTRY

NUMBER 19, PAGES 757-824 5 OCTOBER 1998



Combinatorial chemistry: winning the chemical lottery

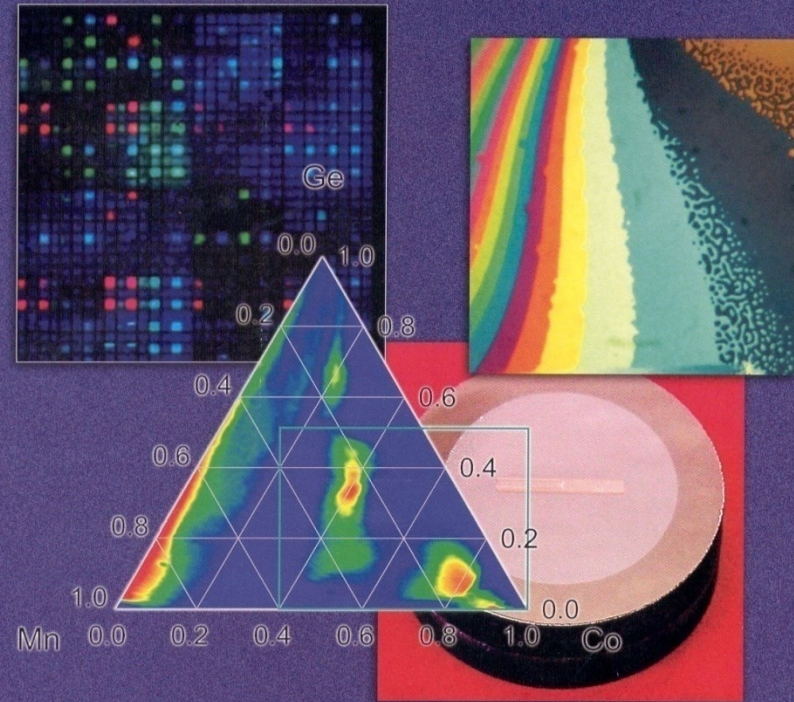
MRS BULLETIN

Serving the International Materials Research Community
A Publication of the Materials Research Society

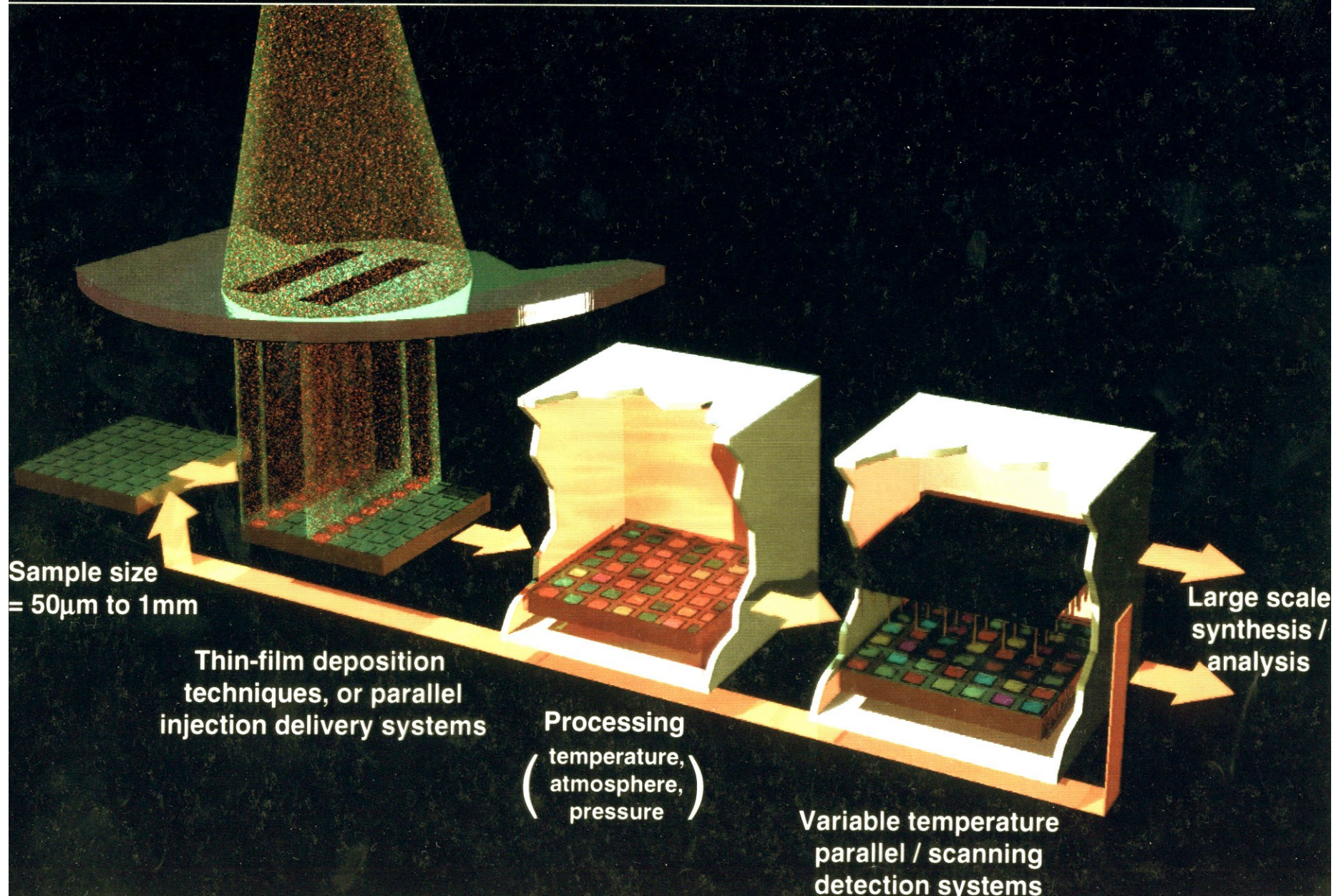
April 2002, Volume 27, No. 4



Combinatorial Materials Science

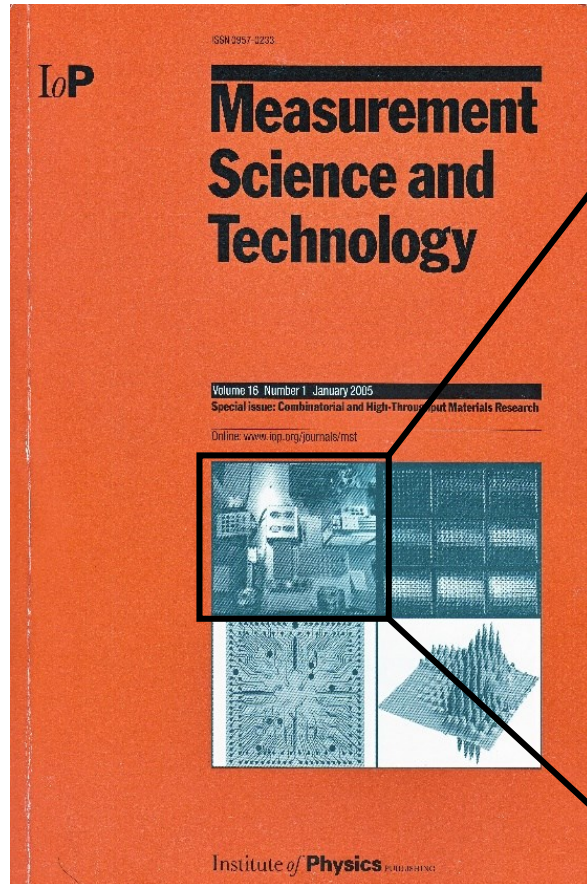


COMBINATORIAL APPROACH TO MATERIALS



COMBIG & COMBIT – micropipette dispensing system (High-throughput powder preparation by solution processing)

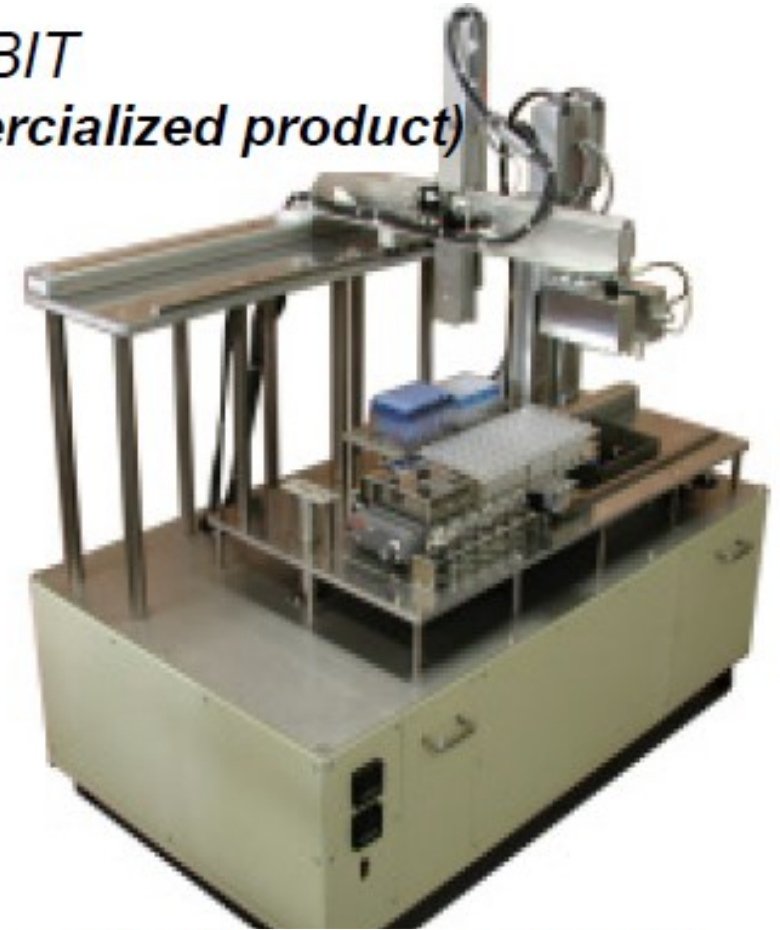
COMBIG (prototype)



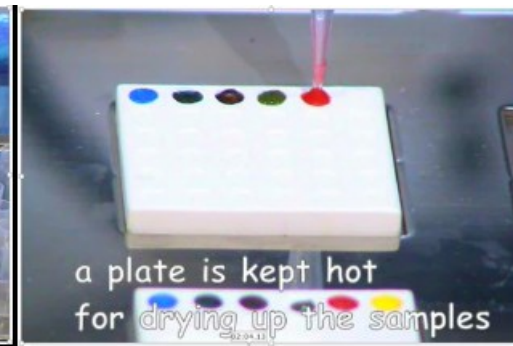
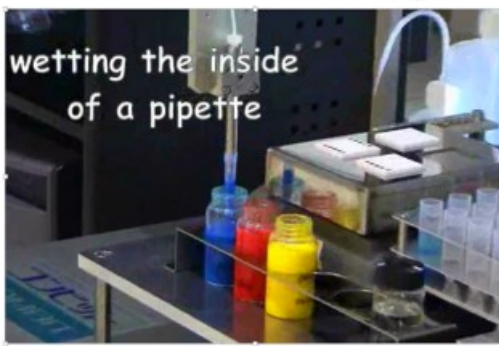
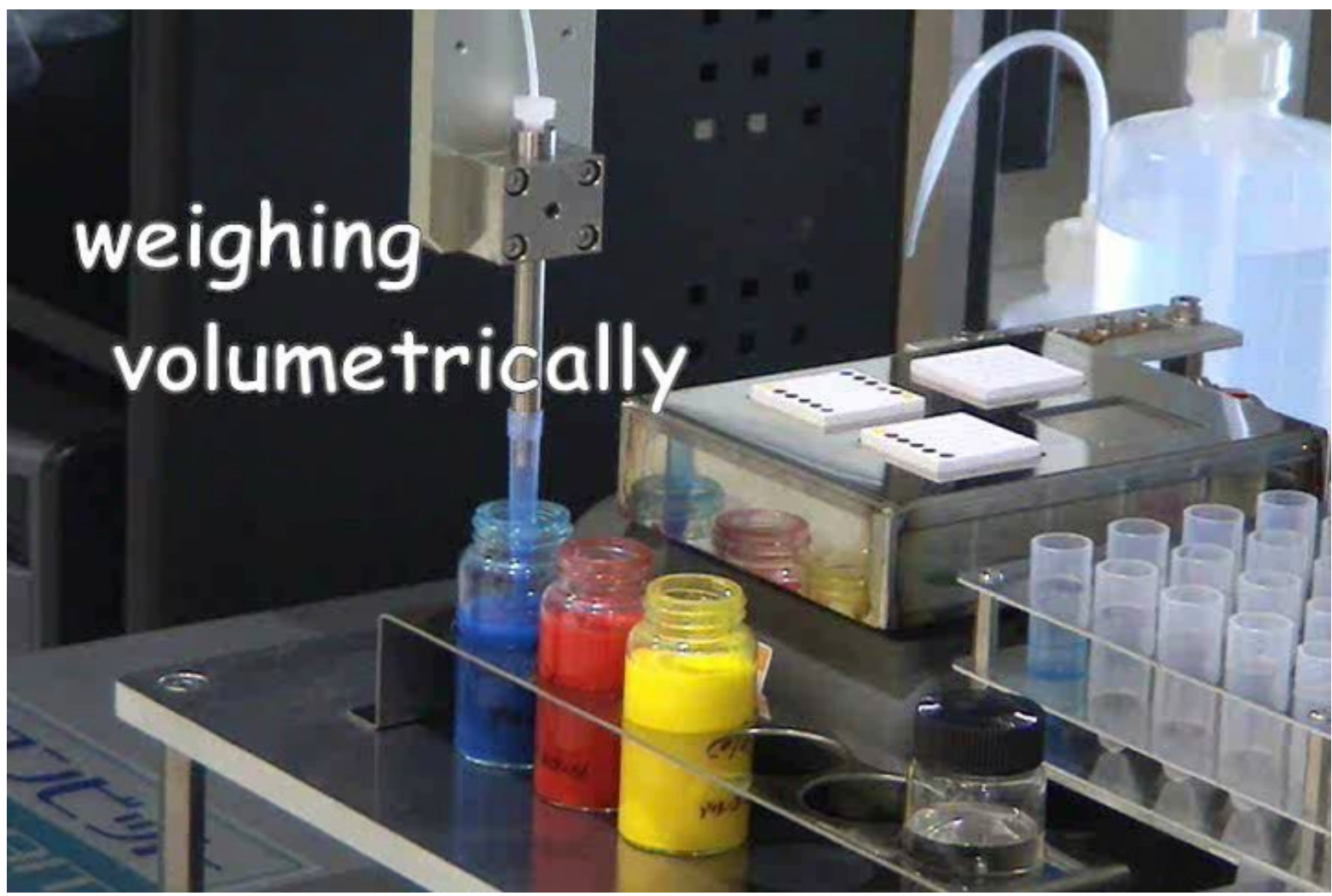
K. Fujimoto and M. Watanabe,
Measurement Science and Technology 16, (2005) 41-45.



COMBIT
(Commercialized product)



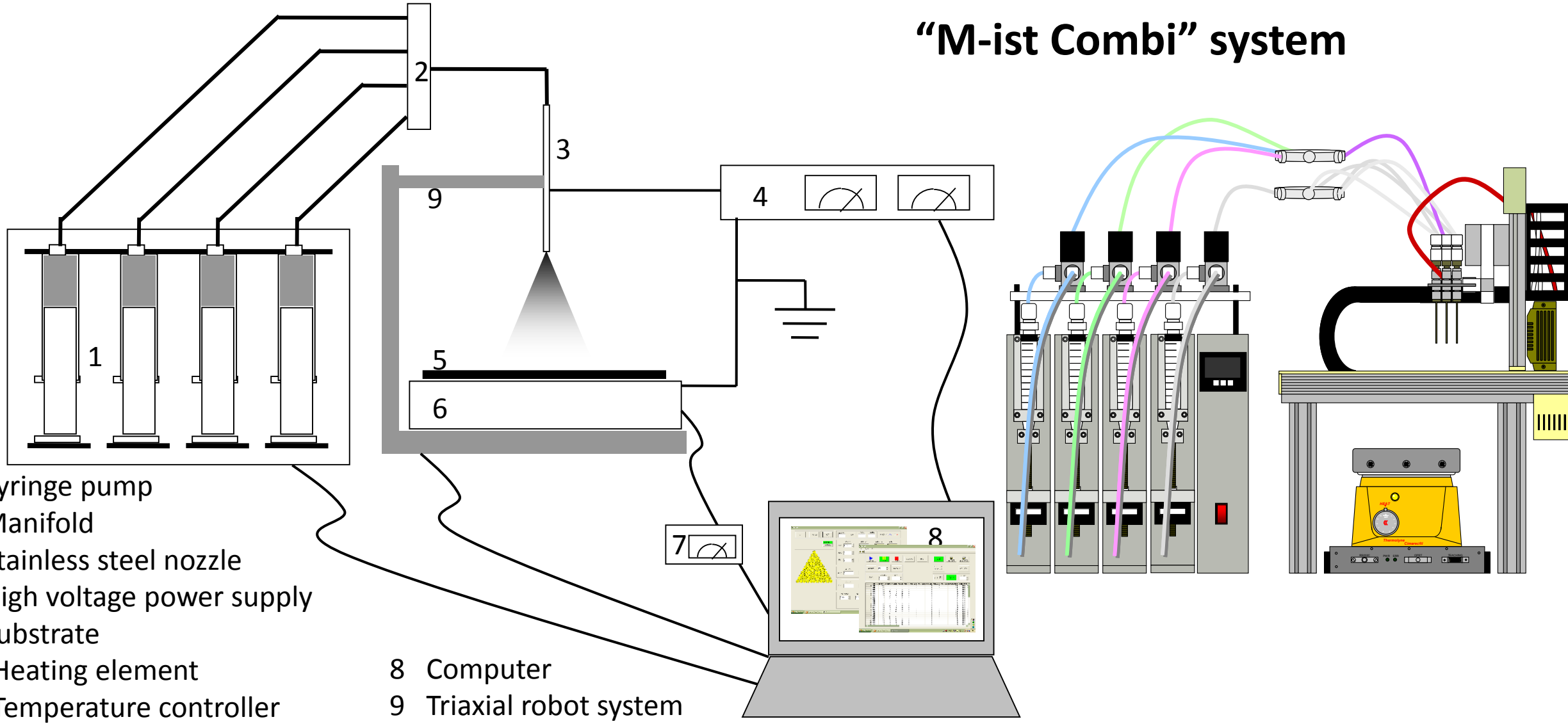
S. Suehara, T. Konishi, K. Fujimoto, T. Takeda,
M. Fukuda, M. Koike, S. Inoue and M. Watanabe,
Applied Surface Science 252 (2006) 2456-2460.



Combinatorial Electrostatic Spray Deposition System

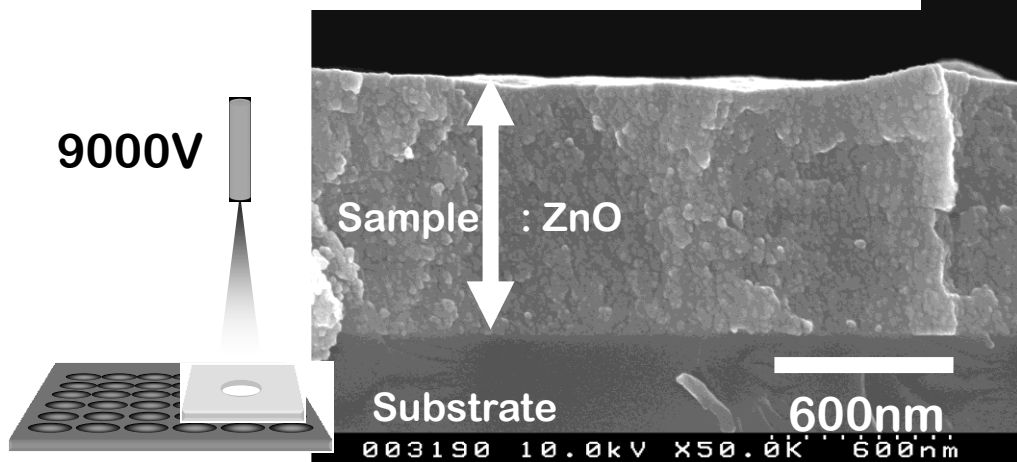
- Atomized mixture solution by applying high voltage is able to deposited as powder or film formation on a grounded and heated substrate.

“M-ist Combi” system

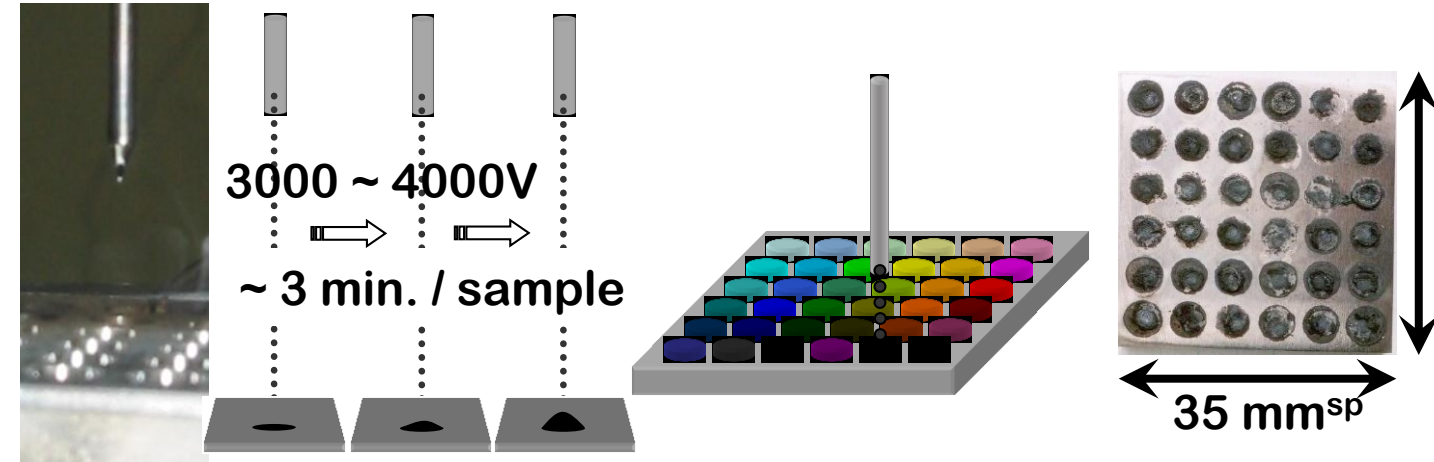


Various preparation mode by "M-ist Combi" system

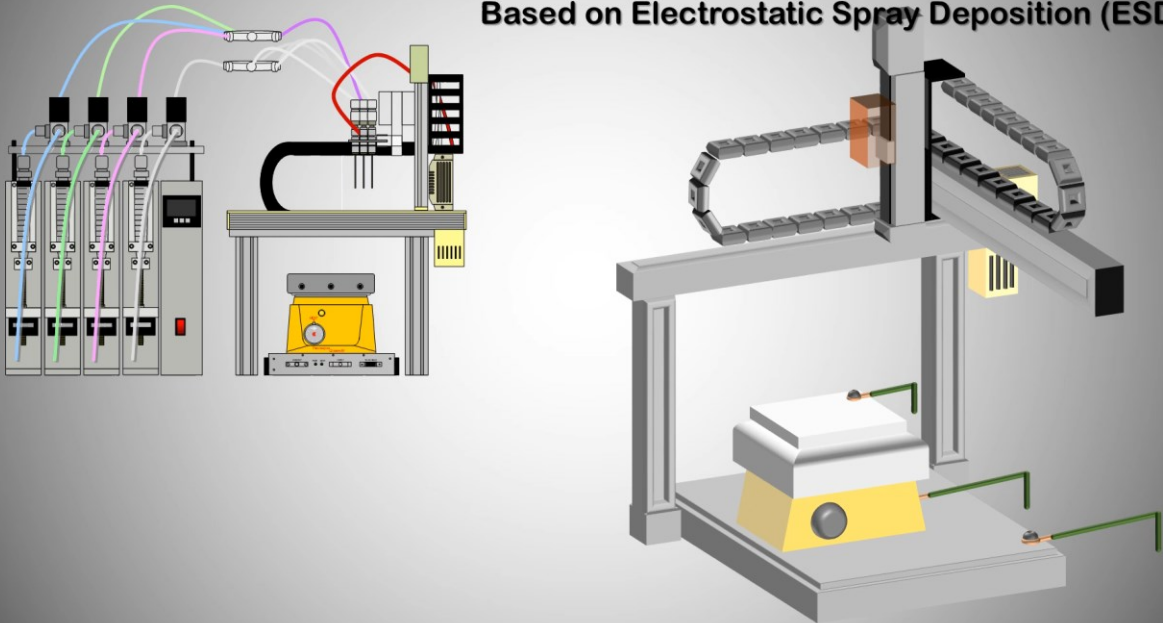
Thin film library preparation mode



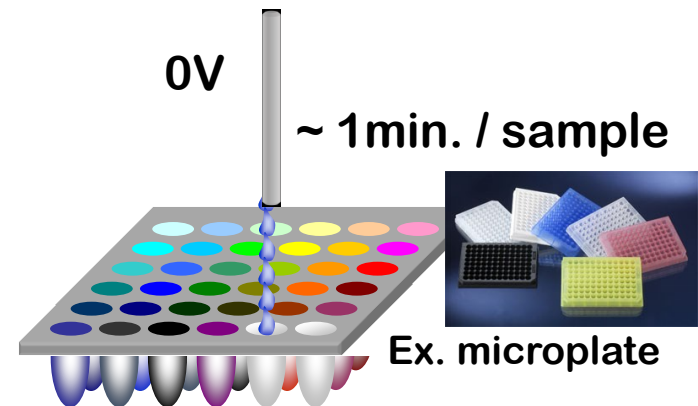
Powder library preparation mode



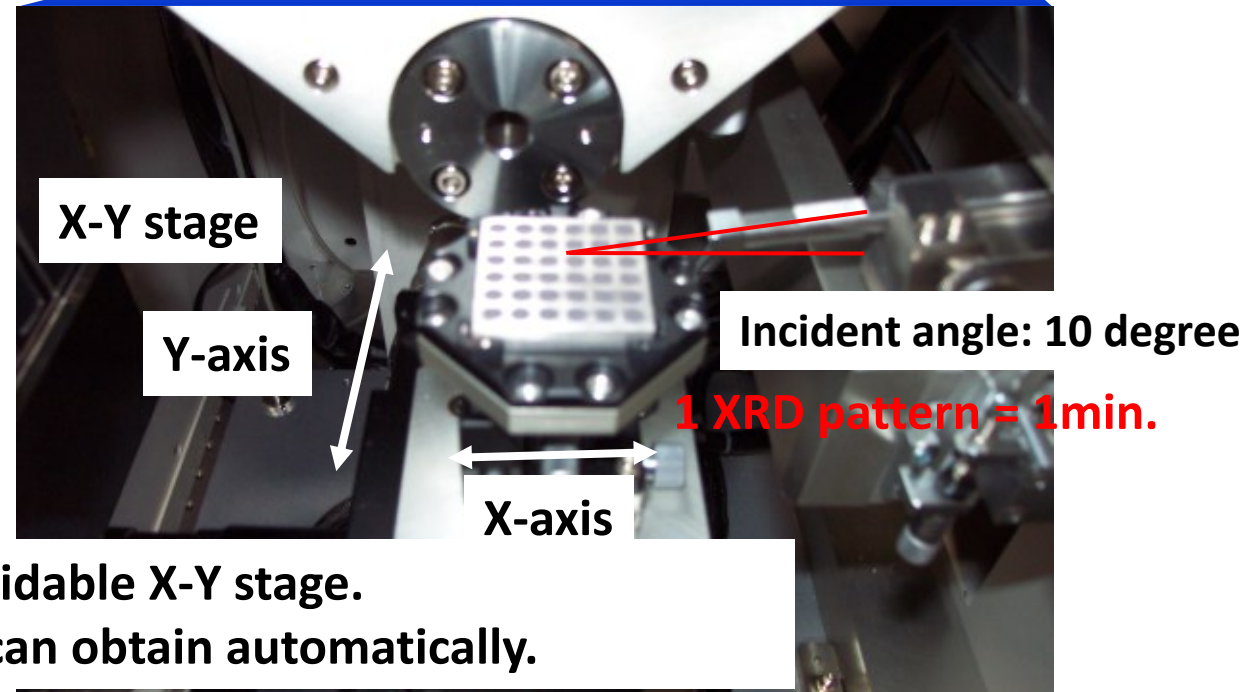
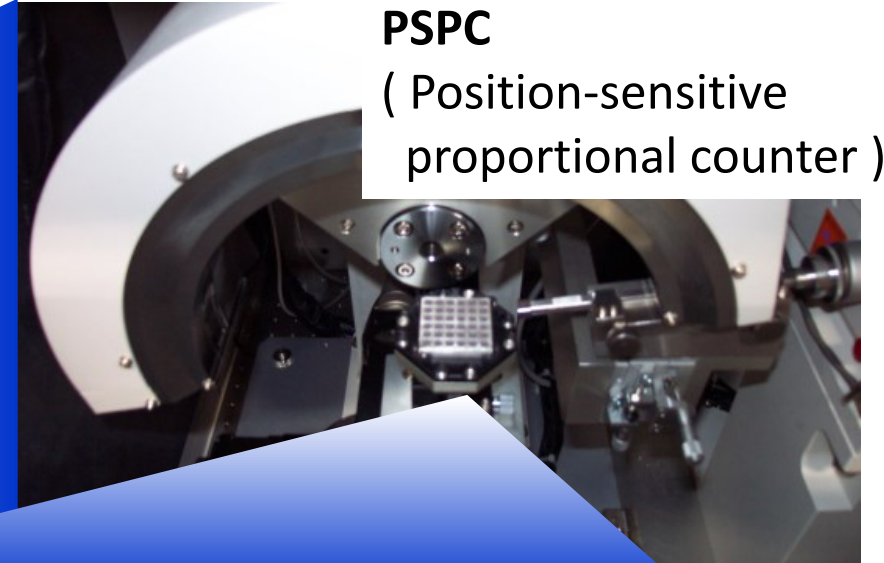
High-throughput Materials Exploration System (M-ist COMBI) Based on Electrostatic Spray Deposition (ESD)



Liquid library preparation mode



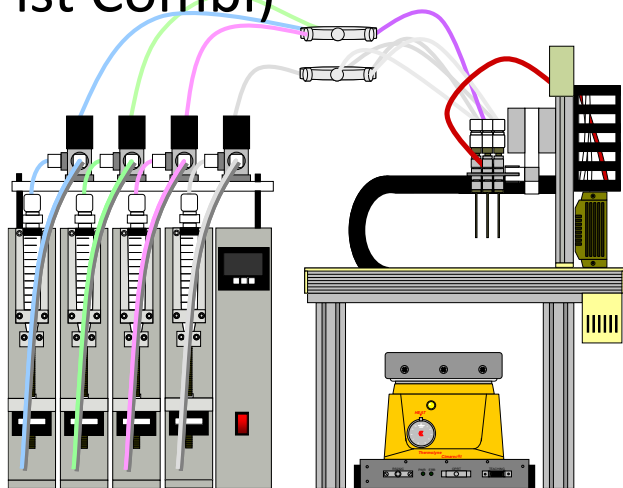
Combinatorial high-throughput XRD System in laboratory level



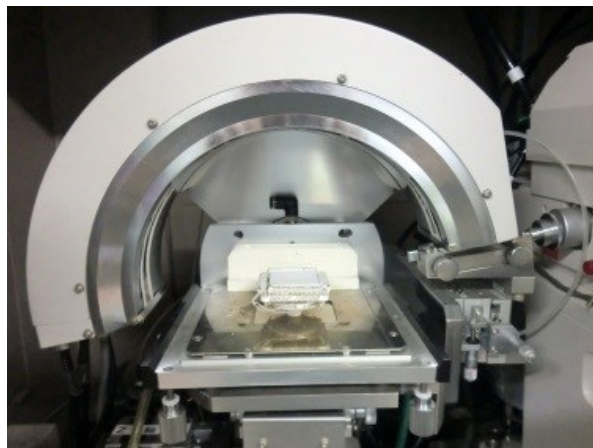
- Reaction plate can put directly on the slidable X-Y stage.
- A number of X-ray diffraction patterns can obtain automatically.

High-throughput functional materials exploration

Powder Library preparation
(M-ist Combi)



Phase identification
(High-throughput XRD)



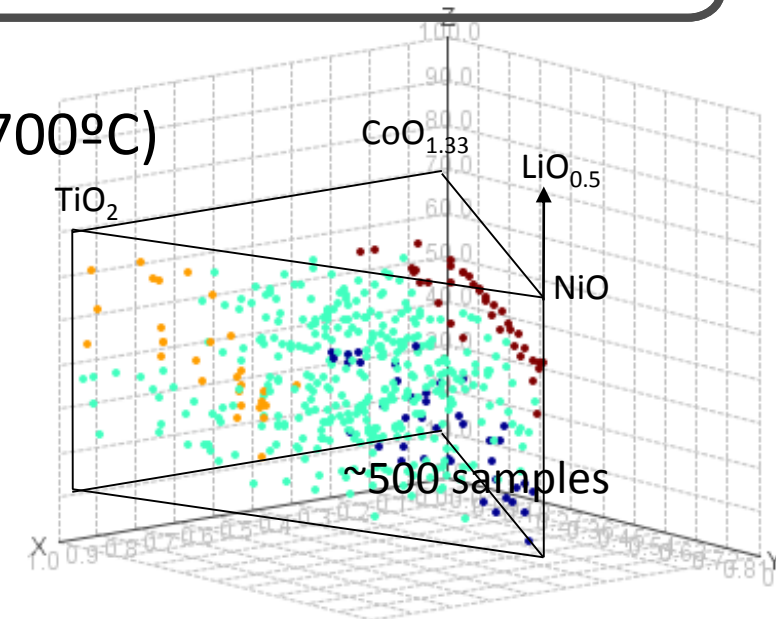
Resolution : c.a. 0.03°

Composition analysis
(ICP, XRF etc.)



Pseudo quaternary Li-Ni-Co-Ti oxides reaction phase diagrams (@700°C)

- single phase of layered-type structure
- single phase of spinel-type structure
- single phase of rock salt-type structure
- multi phase compound



“Combiview” program; C. J. Long, et al., Review of Scientific Instruments 78 (2007), 072217.

“XRDSuite” program; I. Takeuchi, et al., Review of Scientific Instruments 76 (2005), 062223.

K. Fujimoto et al., Mater. Res. Soc. Symp. Proc. 1024E, 1204-A01 (2008).

試料作製が高速化されても・・・

評価と解析に時間が掛かってはハイスループットの効果は半減する。

- ✓ 評価： 放射光での粉末X線回折測定に必要なキャピラリー充填で
キャピラリー(と同じタイミングで心)が折れる作業を減らす
- ✓ 解析： リートベルト構造精密化で一向に収束しない(ストレスが溜まる)
ことのないようにする

には、「楽しんで効率よく正しいデータを出すための！」 手間を惜しまぬ開発(矛盾?)が必要

