High throughput rapid sintering and dielectric characterization of ferroelectrics predicted by machine learning

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I. Overview

Conventional material synthesis and characterization workflows are slow, laborious, and not preferable in the era of big data due to numerous manual processes and experimental variables involved.[1] These constraints can be conquered by developing **automated materials discovery platforms**, ideally in a full cycle (Self-driving) from machine learning (ML) composition screening, to cobot synthesis and high-throughput (HTE) characterization. Here, we describe a proof-of-concept platform to perform HTE rapid sintering and dielectric characterization of tunable materials in the order of minutes per material, as compared to conventional procedures that may take hours or days. Via the rapid sintering a new material structure is revealed for Barium Titanate ferroelectric. The versatility of this approach is demonstrated by screening disordered perovskite materials. We envision that this robotic platform can potentially provide a route to sustainable and large-scale material manufacturing.

II. Introduction

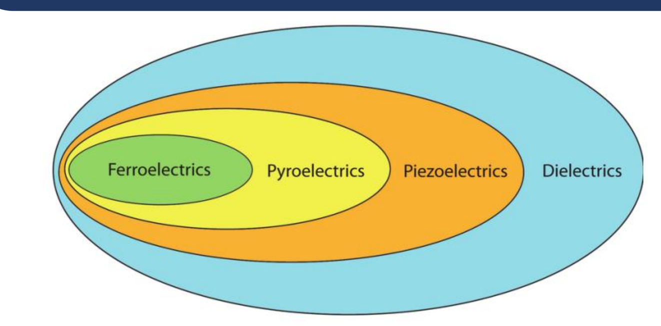


Fig.1 The relationship among the piezoelectric, pyroelectric, and ferroelectric materials

- **Bulk Ferroelectric materials?**

- Subgroup of dielectrics and programable electromagnetics
- Exhibit a spontaneous electric polarisation that can be reversed by the application of an **external electric field or temperature**
- Applications: 5thG cellular networks, flexible biosensors, capacitors, antennas

The primary objective is to discover materials that have:

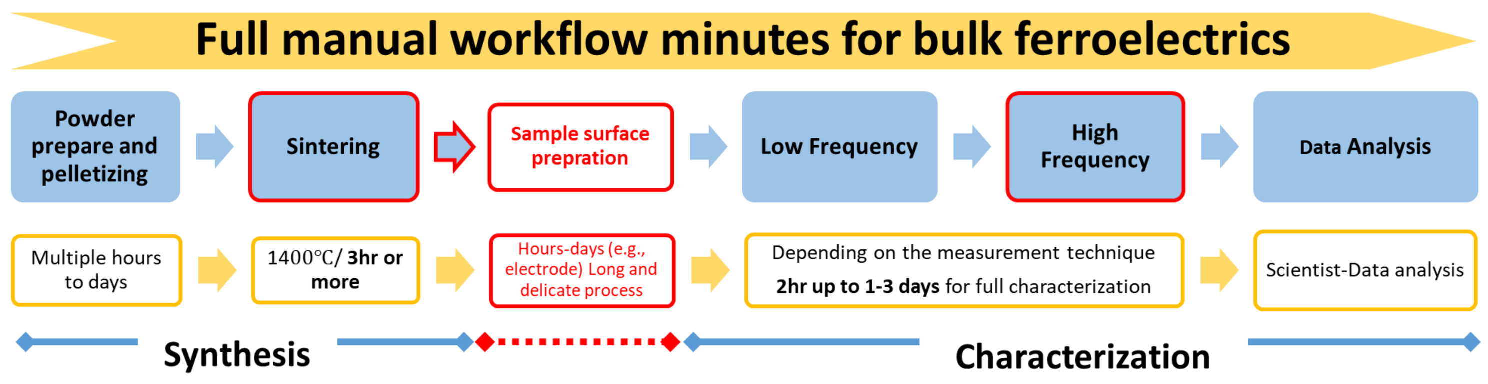
Single phase + **High** permittivity (ε_r) + **High** tunability (τ) + **Low** loss tangent (tan δ)

at high frequencies

$$\tau\ (\%) = \frac{\varepsilon_r(0) - \varepsilon_r(E)}{\varepsilon_r(0)} \times 100$$

where $\varepsilon_r(0)$ is relative permittivity when the field/ temp E=0, and $\varepsilon_r(E)$ is when the electric field E/ temp is applied.

Issue: Synthesis variable governs structure and structure governs properties



- **Down sides of manual solid-state reaction (SRR)**

X Total number of possible compositions = high as a googol (10^{100})

X Experimental validation of ML-predicted compositions = multiple synthesis variables

X Sintering time is long and not energy efficient

X Studies have optimised single steps but linking for autonomous platform has bottlenecks

X **Dielectric testing** at GHz is requires adding metallic electrodes on the surface

X Linking steps, brittleness of samples, difficult for robot to execute without defects

III. Methodology and evaluation

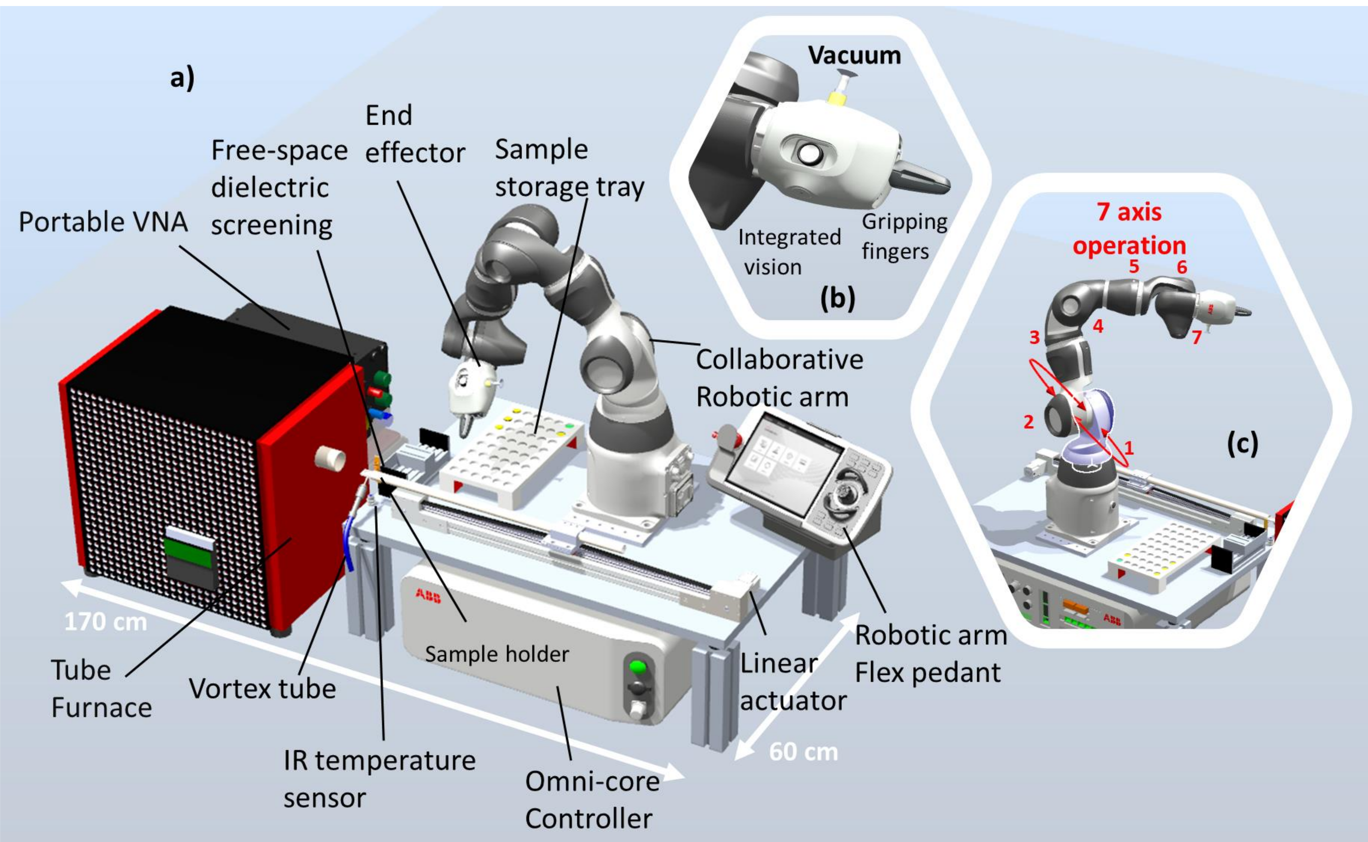
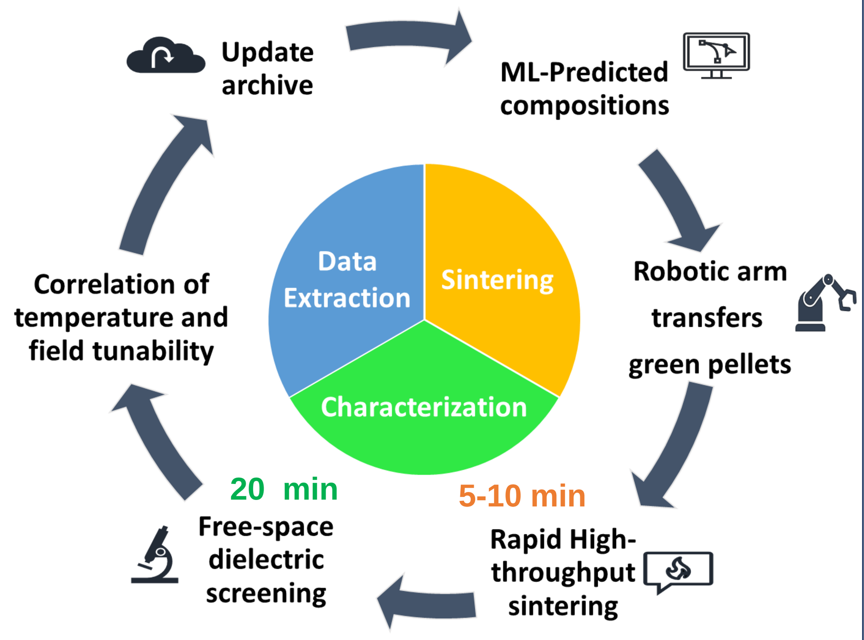


Fig.2 Robotic laboratory for high-throughput synthesis and characterization. a) Digital representation of the automated platform designed for high-throughput rapid sintering and free-space dielectric screening of bulk ferroelectrics C Programing.

- **Automated workflow :**

1. Robotic arm transfers green pellets to a furnace.
2. Rapid sintering for finding the optimum processing condition.
3. Automated temperature tuning sensor for **dielectric screening** at 0.2-3GHz frequency = **allows the robot to detect samples with higher temperature tunning** with no sample preparation required.



Samples	15mm diameter disc
B site doped BST	$(Ba_{0.6}Sr_{0.4}Ti_{0.98}B_{0.02}O_3)$
Ratios of BTS	$(BaTi_{1-x}Sn_xO_3)$
ML-predicted perovskites	Density functional theory (DFT)

- DFT is used to assess the chemical stability & synthesisability of perovskites.[2]
- Compositions with E_{hull} < 0.050 eV/atom were considered potentially single phase

- Sensor is simulated using CST software
- It excites & measures the resonant frequency of the TM020 modes in samples
- The resonant frequency is directly related to the permittivity of the sample

Human intuition-driven manual workflow is applied to evaluate the benefits and gaps of the automated platform setup:

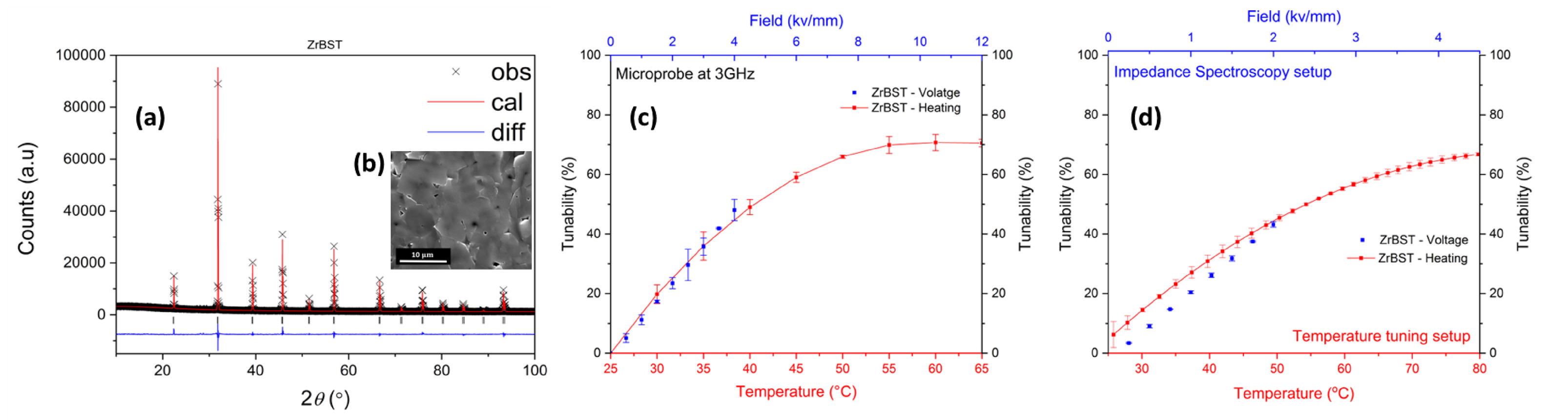


Fig.3 (a) Rietveld fitted XRD patterns, **(b)** SEM image (10 μm), **(c)** High Frequency (3GHz) CPW, and **(d)** Low Frequency (100kHz) for ZrBST.

IV. Results

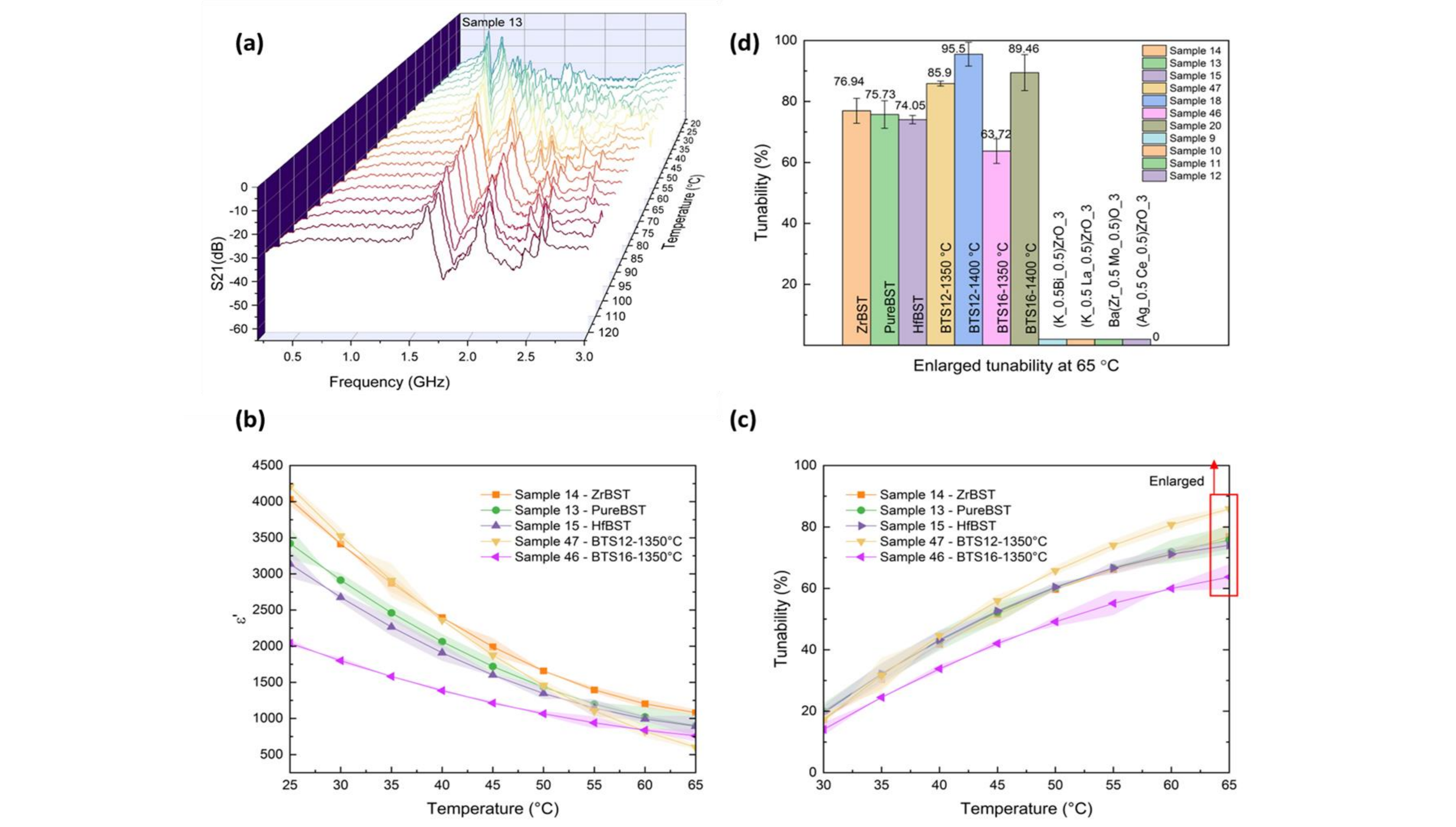
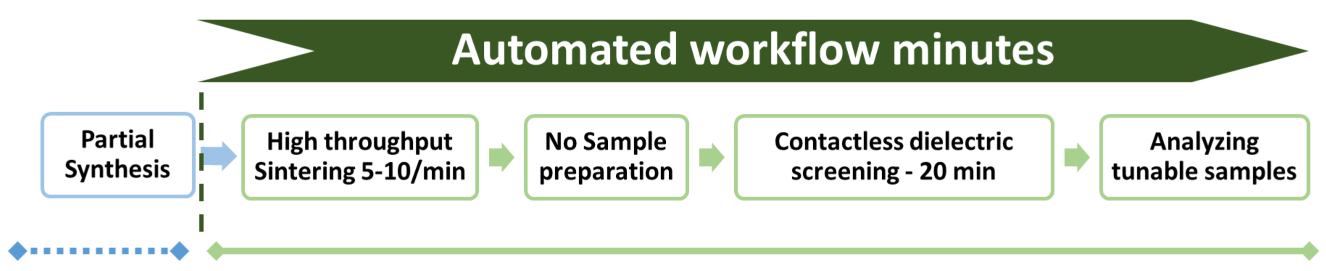


Fig.4 a) Shift in transmission response (S21) during temperature change (120-20°C) for a random sample, b) thermal variation of tunability for 5 selected samples (ZrBST, PureBST, HfBST, BTS12-1350°C, and BTS16-1350°C), c) thermal variation of tunability for 5 selected samples, and d) tunability percentage values at 65°C

- Automated setup characterised all 52 rapidly sintered samples over a temperature range of **120 to 25°C**.
- Results show 80% correlation with CPW high frequency measurements.
- After rapid sintering 7 BTS green pellets in 70 min, in a temperature range of 1100-1400°C, the optimal sintering temperature for achieving full density was found to be 1350°C for BTS family
- A new material structure is revealed for BST, which possesses peculiar tuning performance with a hybrid and simultaneous thermal/electrical bias.



V. Conclusion and Future work

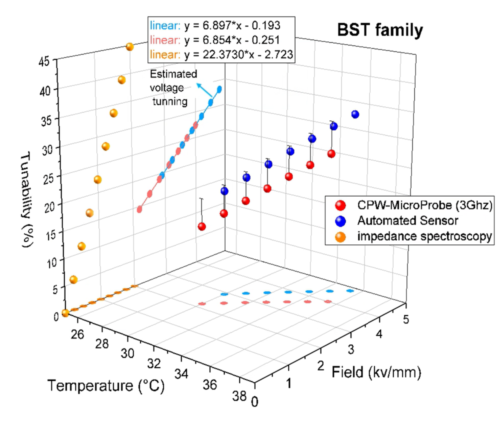


Fig.5 The correlation between temperature, field, and tunability for the BST family, comparing the sensor CPW.

A HTE workflow is developed for synthesising and characterising bulk ferroelectrics by connecting sintering and high frequency measurement steps with no sample preparation required. Rapid sintering reviled optimized dielectric tunability and decreased tanδ with increased sintering temperature BTS family. A limitation is the manual sample preparation prior to sintering, however recent studies have achieved in-situ powder mixing and rapid experimental alloy development,[3] which potentially can be combined for a fully autonomous discovery. This could potentially lead to sustainable and large-scale material manufacturing.

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References

[1] H. Zhang, H. Giddens, Y. Yue, X. Xu, V. Araullo-Peters, V. Koval, M. Palma, I. Abrahams, H. Yan, Y. Hao, J Eur Ceram Soc 2020, 40, 3996.
[2] A. Ihalage, Y. Hao, NPJ Comput Mater 2021, 7, 75.
[3] K. S. Vecchio, O. F. Dippo, K. R. Kaufmann, X. Liu, Acta Mater 2021, 221, 117352.