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Multi-Principal Rare-Earth Substitution and Entropy Effects in $BiFeO_3$: Structural, Dielectric, and Magnetic Properties

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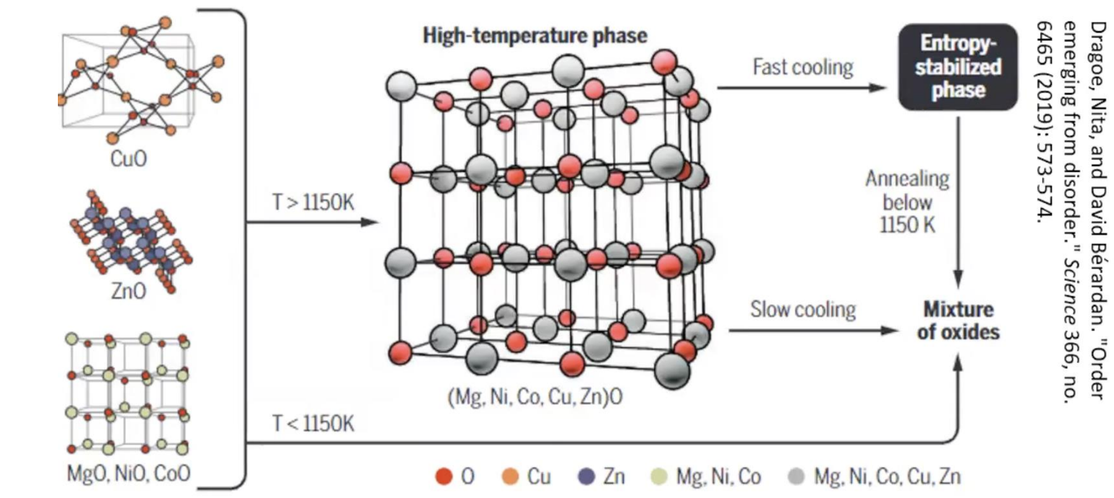
INTRODUCTION & AIM

$BiFeO_3$ (BFO) is a well-known room-temperature multiferroic, combining ferroelectric and magnetic order. Its practical application is limited by phase instability, high leakage, and weak magnetization.

Entropy engineering, based on multi-principal cation substitution, provides a new route to stabilize complex oxides. By increasing configurational entropy on the A-site, disorder can lead to thermodynamic stabilization and enhanced functionality.

Aim: To explore the configurational-entropy effects in BFO through multi-element rare-earth (RE) substitution and to correlate phase stability with dielectric and magnetic properties.



Dragoe, Nita, and David Bérardan. "Order emerging from disorder." *Science* 366, no. 6465 (2019): 573-574.

ENTROPY ENGINEERING — "ORDER FROM DISORDER"

- Entropy-stabilized materials exploit the term $-T\Delta S_{mix}$ in the Gibbs free energy equation ($\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$) to counteract enthalpic destabilization.
- The multi-principal approach creates numerous possible combinations and stoichiometries, offering tunability by simply exchanging or adjusting RE elements.
- This work applies that concept to **$Bi_{0.9}(RE)_{0.1}FeO_3$** (RE = La, Nd, Gd, Eu, Y), representing an **entropy oxide** designed for improved crystallinity and multifunctional response.

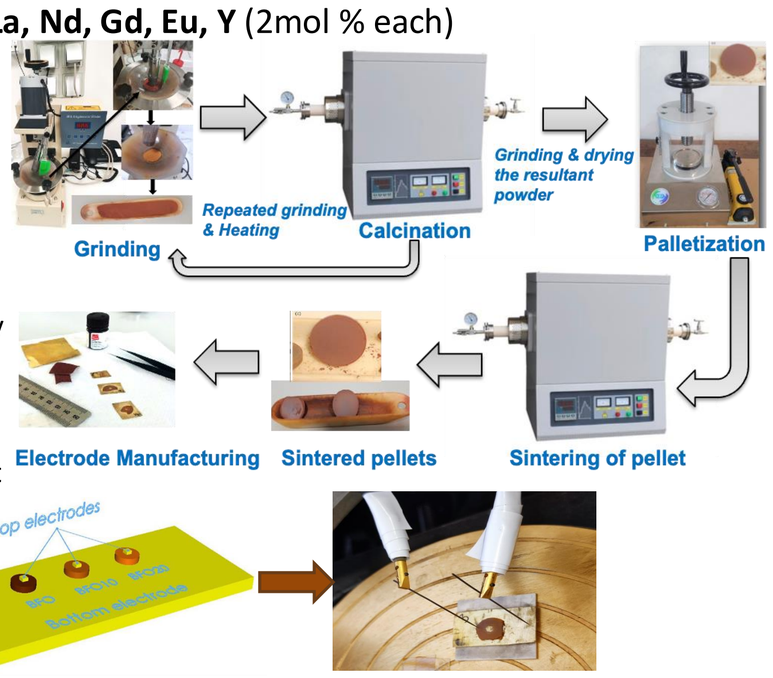
METHOD

Composition

$Bi_{0.9}(RE)_{0.1}FeO_3$, where **RE = La, Nd, Gd, Eu, Y** (2mol % each)

Synthesis

- Conventional solid-state route.
- **Pre-calcination:** 600 °C (1h)
- **Sintering:** 950 °C and 1000 °C



Characterization/Analysis

- ✓ **XRD** → Phase purity, crystallinity
- ✓ **SEM** → Grain morphology, and density
- ✓ **VSM** → RT magnetic hysteresis
- ✓ **LCR meter** → Dielectric constant (ε′), loss tangent (tan δ), & AC conductivity (σ)

ENTROPY CALCULATION

The configurational (mixing) entropy, ΔS_{conf}, was estimated using:

$$S_{conf} = S_{mix} = -R\sum_{n=1}^{i} x_n \ln x_n$$

- ΔS_{mix} is the mixing entropy also called configurational entropy (ΔS_{conf})
- R is the gas constant.
- x_n is the mole fraction of each component present in each site (A-site, B-site and O-site) of sublattice in solid solution and ln is the natural logarithm.

The x_n values can be calculated based on the stoichiometry of the material. For $Bi_{0.9}(RE)_{0.1}FeO_3$, with $X_{Bi} = 0.9,\ X_Y = X_{Eu}, X_{La}, X_{Nd}, X_{Gd} = 0.02$ *each and* $X_{Fe} = 1$

Substituting these values into the formula to calculate the mixing/configurational entropy:

ΔS_{conf} = 4.048 J mol^{-1} K^{-1} = 0.486R = 0.486K$_B$ per A-site atom

This value places the composition in the **moderate to High entropy oxide** regime, confirming significant A-site configurational disorder contributing to phase stabilization.

As per empirical classification, by Murty et al., **ΔS_{conf} ≥ 1.5R classified as "high entropy".**

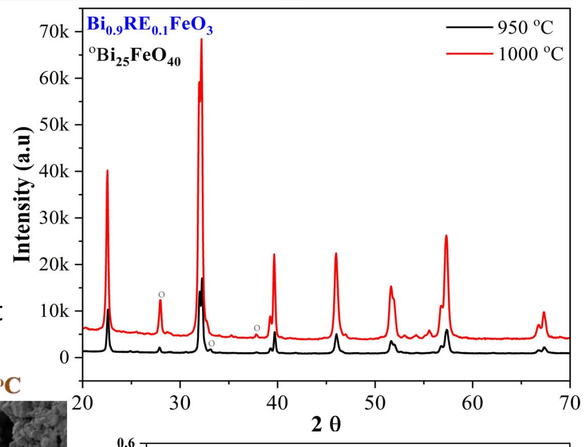
RESULTS & DISCUSSION

STRUCTURAL ANALYSIS

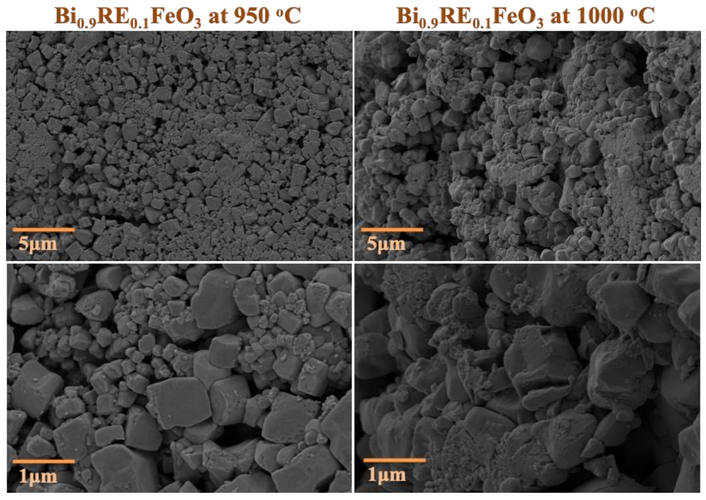
XRD: Perovskite phase stabilized at both 950°C & 1000°C.

Sharper peaks and reduced impurities at 1000 °C with 97% of BFO phase (rhombohedral (R3c))

→ **improved crystallinity.**



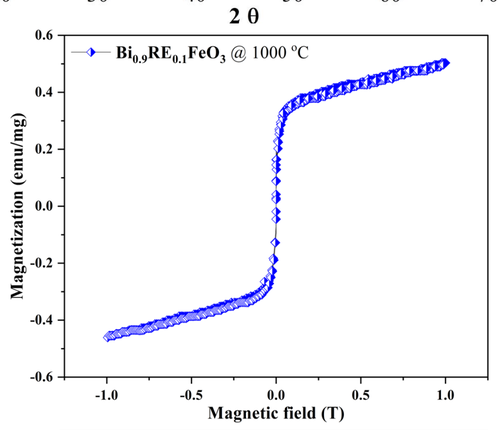
SEM: Densely packed, uniform grains observed at 1000°C indicating reduced porosity

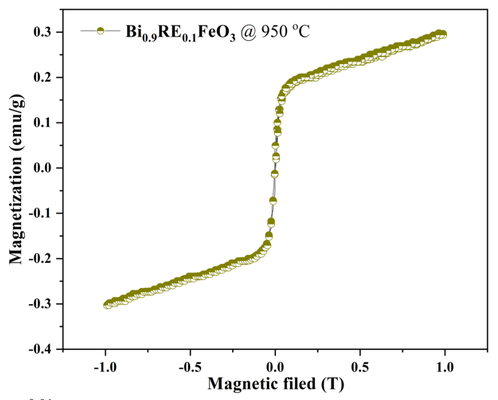


FUNCTIONAL PROPERTIES

Magnetism:

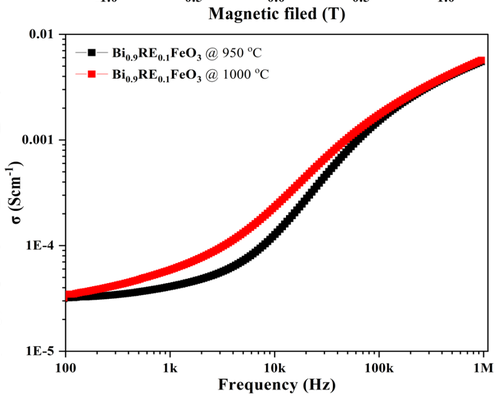
- M–H loops (RT, ±1 T) show weak ferromagnetism.
- **Hc:** 80–120 Oe; slightly higher at 1000 °C.
- RE-induced **A-site disorder** and **spin canting** disrupt the cycloid, increasing net moment.
- Entropy-driven structural distortion further enhances magnetic response

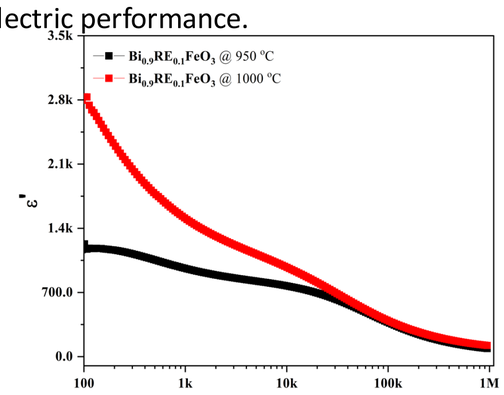


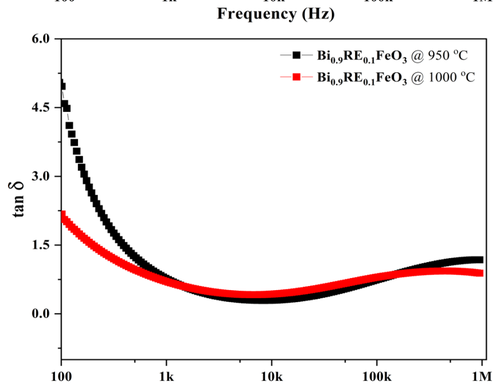


Dielectric Response:

- **ε′** increased from ~960 → ~1500 at 1 kHz (950 °C → 1000 °C). While **tan δ** decreased from 0.77 → 0.69 indicating reduced leakage at 1000 °C
- **σ_{ac}** slightly rose (4.05×10^{-5}→5.08×10^{-5} Scm^{-1}) perhaps due to Fe^{2+}/Fe^{3+} hopping and O_2 vacancies. **This means that S_{conf}** from multi RE substitution, combined with optimized sintering, enhances structural stability, grain connectivity, and magneto-dielectric performance.







CONCLUSION

- Multi-principal RE substitution effectively stabilizes the perovskite phase of $BiFeO_3$.
- Entropy-driven structural order enhances dielectric constant, reduces losses, and induces weak ferromagnetism.
- $Bi_{0.9}(RE)_{0.1}FeO_3$ synthesized at 1000 °C shows a balanced combination of crystallinity, low leakage, and functional performance.
- The approach validates entropy engineering as a scalable route to multifunctional oxides.

FUTURE WORK / REFERENCES

- Extend RE substitution beyond five cations to explore higher-entropy limits.
- Perform temperature-dependent dielectric and magnetic studies.
- Integrate with theoretical modeling of entropy-stabilized perovskites.

References:

1. Rost, C.M. *et al.*, *Nat. Commun.* **6**, 8485 (2015).
2. Sarkar, A. *et al.*, *Nat. Rev. Mater.* **3**, 187 (2018).
3. Aziz, S. *et al.*, *Magnetochemistry*, ***10***(8), 60 (2024)
4. Witte, R. *et al.*, Phys. Rev. Materials **3**, 034406 (2019)