nature portfolio

Peer Review File

Entropy Engineering for Advanced Microwave Ceramics

Corresponding Author: Professor Yuan-Hua Lin

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The manuscript entitled “Designable Microwave Dielectric Ceramics via Entropy-driven Oxygen Octahedral Modulation” by Jinquan Zeng et al. investigates the modulation of microwave dielectric ceramics for antenna applications through configurational entropy engineering. This approach provides an effective strategy to simultaneously optimize the key dielectric parameters (ε_r, Q×f, and τf) by collectively regulating cation displacement, octahedral distortion, and M–O bond covalency. The entropy-driven structural modulation enables synergistic property tuning and helps overcome conventional trade-offs. The optimized $NiNb_2O_6$-based medium-entropy ceramic exhibits $\varepsilon_r \approx 22.3$, Q×f ≈ 140,000 GHz, and a near-zero τf (–14.8 ppm/°C). Furthermore, a prototype antenna demonstrates broadband operation (5–8.5 GHz) with energy efficiency exceeding 99.98%.

The manuscript is well written and presents significant results; however, some queries and minor modifications need to be addressed before it can be considered for publication. Since the novelty of this work lies in the modulation of microwave dielectric properties through configurational entropy induced by multiple cation substitution, further clarification and discussion regarding the role, quantification, and physical implications of configurational entropy are required. In particular, the authors should clearly explain how configurational entropy is calculated, how it correlates with the degree of cation disorder, and how this disorder influences the dielectric response in the microwave frequency region. A more detailed discussion will help to better establish the structure-entropy-property relationship and strengthen the novelty and scientific rigor of the manuscript.

1.The discussion on configurational entropy in the Introduction is not sufficient. The authors should elaborate on its physical significance, particularly why configurational entropy is important and how it influences dielectric behaviour and property modulation in the microwave frequency region. A clearer explanation of the underlying mechanisms linking entropy to dielectric polarization, loss, and structural dynamics would improve the scientific depth and clarity of the manuscript.

2.The description of the DFT calculations in the Supplementary Information is not sufficiently clear. The authors should explicitly explain the computational methodology, particularly how the crystal structures with multiple cation species were constructed. It is unclear whether the cation distribution was modelled within a unit cell or by constructing supercells. If the calculations were performed using the crystal structure shown in Fig. 1, clarification is needed on how multiple cations were accommodated at specific lattice sites, since such disorder cannot be directly represented within a single ordered unit cell in standard DFT calculations. A detailed explanation of the structural model, cation configuration strategy (e.g., ordered approximation, supercell approach, or special quasi-random structures), and computational parameters would improve the credibility and reproducibility of the results.

3.In Figure 3, the authors present the evolution of M–O covalency as a function of configurational entropy using experimental techniques such as temperature-dependent Raman, EXAFS, and Nb K-edge XANES. Although these methods provide indirect evidence of O 2p–Nb 4d hybridization, more direct verification would strengthen the conclusions. The authors are encouraged to provide DFT-based electronic structure analysis, such as partial density of states (PDOS), to directly demonstrate the degree of orbital hybridization. In addition, XPS analysis could offer further experimental evidence of the covalent character and would complement the interpretation of the entropy-driven covalency modulation.

Reviewer #2

(Remarks to the Author)
This is an interesting effort to arrive at a means to achieve a difficult set of combination of parameters to make a material suitable for microwave dielectric resonators, namely high dielectric loss, low loss and low value of temperature coefficient of resonant frequency.
1. But the authors achieved a set of values as ϵ' ~22.3, Q×f (~140000 GHz), and τf (-14.8 ppm/oC) in $NiNb_2O_6$.
However it is far less impressive the dielectric resonator available in the dielectric constant range around 25.
Nomura, S., Toyama, K., & Kaneta, K. (1982). "Ba(Mg1/3Ta2/3)O3 Ceramics with Temperature-Stable High Dielectric Constant and Low Microwave Loss." Japanese Journal of Applied Physics, 21(10), L624. They report the following set of parameters in 1982 itself:
Dielectric Constant:25
Quality Factor : 17,600 (at 10 GHz), Q.f 176,000 GHz
Temperature Coeff: 4 ppm/°C
Later other workers reduced the τf of this composition to ~0 to 0.5 ppm/°C (Peng et al., 2023).
Therefore, after nearly half a century, what is claimed by the present authors as a great combination of results is not so.
2. A DRA is fabricated for demonstrating the superiority with this composition. However any dielectric resonator with these set of material parameters will give the same response with the chosen design. It has nothing to with the composition.
3. "As shown in Figs. 4a, the ε_r increases monotonically with configurational entropy, rising from 21.6 in low-entropy compositions to 23.3 in the high-entropy variant." The compositions vary widely to achieve variation in configurational entropy. That will result in different sinterability and resulting in differences in final densities, grain size, grain boundaries etc for the resulting compositions. The narrow range of dielectric constant variation can easily because of these extraneous factors. It is very difficult to correlate these small changes to intrinsic factors like changes in configurational entropy. In ensembles where the variation is so large that the variations can be solely attributed to intrinsic factors, the proposed hypothesis can be tested.
4. "Q×f exhibits non-monotonic behavior, peaking at ~140,000 GHz in the medium-entropy composition before declining at higher entropy (Fig. 4c). This mirrors the covalency maximum observed by calculation prediction and covalency validations, indicating that optimal Nb-O orbital hybridization at intermediate entropy minimizes intrinsic dielectric loss by suppressing anharmonic phonon scattering." The loss factor is quite sensitive to both intrinsic and extrinsic factors which are well studied by Kamba et al. In each of the compositions considered in the Fig.4c, the reason for the variation in Q value could be quite different. It is known that increased covalency will lock up the ions to minimize the lattice vibration based intrinsic loss. Since a wide range of intrinsic and extrinsic parameters are responsible for the variation of Q factor, attributing the observed variation solely to the configurational entropy is questionable.
5. "τf shifts toward more positive values with increasing entropy, as depicted in Figs. 4b. This improvement arises from entropy-induced octahedral distortion, which strengthens the restoring force for temperature-dependent tilting modes of the [NbO6] framework, thereby stabilizing resonance against thermal fluctuations." In this case also for each composition, the origin of the τf depends on cancelling the effect of thermal expansion with the effect of permittivity variation with temperature. Multiple factors are involved and simply attributing the observed changes only to configurational entropy is not justified. First of all, such small changes need not be completely intrinsic in origin. We are dealing with ceramics which are sintered at high temperature. They are bound to have oxygen vacancies. Without considering all the associated factors, we can not attribute the entire changes to configurational entropy.
6. However configurational entropy is a key parameter and it can guide material engineering, if the influence of each parameters are carefully understood and controlled. It is better done in systems where extrinsic factors are few and their role across composition variation are predictable. In a sintered ceramic system, subtle intrinsic factors get greatly submerged by a wide variety of extrinsic factors which act differently with changes in composition.

Reviewer #3

(Remarks to the Author)
In this work, ANb_2O_6-based ceramics were developed to achieve an optimized relative dielectric constant, ultra-low dielectric loss, and a near-zero temperature coefficient of resonant frequency. The authors introduced configurational entropy as a global index to simultaneously regulate cation displacement, octahedral distortion, and M-O bond covalency, effectively bypassing the intrinsic trade-offs that typically hinder the independent optimization of microwave dielectric parameters. This strategy enabled the fabrication of a prototype dielectric antenna that outperforms state-of-the-art devices. The research topic is significant, the entropy-driven design approach is innovative, and the experimental data are robust. This manuscript meets the scope and standards of Nature Communications and is recommended for publication after the following minor issues are addressed:
1. In the introduction, are there other high-entropy microwave dielectric studies that should be cited to position the present contribution more precisely? Additionally, the connection between configurational entropy and octahedral decoupling would benefit from a bridging statement. The authors explain that entropy expands solubility and preserves single-phase integrity but do not explicitly clarify why this should decouple the εr/Q×f/τf trade-offs.
2. In the experimental procedure section, it would be helpful to specify the elemental composition for each sample (e.g., $Ni_{0.5}Mg_{0.5}$, $Ni_{0.2}Mg_{0.2}Zn_{0.2}Co_{0.2}Mn_{0.2}$, etc.) to avoid ambiguity. Additionally, only four compositions appear to be presented. Is there a missing composition, specifically the one with s=1.39?
3. The term "medium-entropy" is used throughout the manuscript without a precise definition. The boundaries between low-, medium-, and high-entropy classifications should be explicitly defined (e.g., S < 1R as low, 1R-1.5R as medium, and >1.5R as high). Do the authors follow this convention or an alternative one?
4. Figures 1a and 1b appear to be swapped. Please verify that the figure labels are consistent with the corresponding descriptions in the text and captions.

5. The sintering temperature range is reported as 1150-1300°C, but the specific optimal sintering temperature for each composition is not stated. Given that different A-site compositions are likely to have different optimal sintering windows, this information is important for reproducibility.
6. The non-monotonic covalency trend is among the most novel findings in this work; however, the physical explanation remains somewhat unclear. Why does covalency peak at medium entropy and then decrease? The authors attribute this behavior to changes in orbital hybridization, but a clearer mechanistic explanation would strengthen the discussion. For example, is this trend related to competing local distortion effects or to the specific electronic configurations of Co^{2+} and Mn^{2+} introduced at higher entropy levels?
7. The precession electron diffraction (PED)-derived pair distribution functon(PDF) analysis is used to validate DFT predictions of Nb-O bond length changes. However, the manuscript does not discuss the uncertainty or resolution limits of PED-based PDF for distinguishing sub-0.1 Å differences in bond length. A brief discussion of the precision of this technique in this context would strengthen the validity of the claim.
8. What are the A-site elements in $ATiO_3$ and AAl_2O_4? Are they the same elements used in the ANb_2O_6 system?
9. There are typographical errors in the references. For example, "Cream." should be corrected to "Ceram." for ceramics-related journal titles.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have revised the manuscript, and the revisions have significantly improved its quality and scientific significance, providing greater clarity to the presented of results and discussions. Now the manuscript can be accepted

Reviewer #2

(Remarks to the Author)
It is true that the authors tried to do many things in response to my comments (Reviewer 2). They recognize that the comments are quite serious. All the remedial work done are quite good and useful.

But they fail in addressing the central question: Is this the right material system where the proposed hypothesis can be properly tested. Unfortunately the answer is a firm No.

It is a ceramic system where a slight change of composition changes the entire processing variables and hence characteristics, based on very small changes in dielectric characteristics, trying to establish 2 profound concepts involving Entropy-driven Oxygen Octahedral Modulation and covalency is outlandish.

Problem is indeed quite valid. If that is the primary objective, better to choose highly simple material systems where other factors pointed out doesn't come to prominence and hence a correlation can reliably established. Primary variations should be with respect to Oxygen octahedral modulation and controlled changes with associated covalency.

The rest of the studies are interesting and important. With a suitable title the remaining data may be published in an appropriate Materials Engineering Journal. The proposed ideas may be mentioned as
possible reasons. But the template chosen is too poor to establish the grandiose theories proposed.It can not be part of the title.

Authors claim that "our work establishes a complete mechanistic framework connecting configurational entropy directly to microwave performance through octahedral geometry." It is too premature to say that. Certainly not with ceramic compositions showing too small property variations while the changes in the compositions are too great.

The DRA work doesn't prove anything regarding the composition since an Electrical engineering design doesn't see the composition: it sees only the electrical parameters of the device.

"We do not claim configurational entropy is the only factor governing Q×f. Instead, our control experiments have eliminated all major confounding variables, indicating that entropy-modulated Nb-O covalency is the dominant cause of the non-monotonic Q×f trend." Loss is too complicated a subject to be eliminated by a few control experiments as claimed.

"In contrast, the experimentally observed τf evolution matches well with the trend of entropy-induced octahedral distortion measured independently via EXAFS and Raman spectroscopy, but does not correlate with the change in oxygen vacancy concentration" First substract the effect of oxygen vacancies. Then see the trend of the remaining with respect to entropy induced octahedral distortion as the effect of Oxygen vacancies will persist.

Reviewer #3

(Remarks to the Author)

The authors have addressed all my comments

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)
Last line of the abstract is highly deceptive. It is only partially correct. This point was pointed out earlier but it is retained without any change.
“Exploring the microscopic mechanism of complex application-oriented systems is one of the core topics of materials research, and its academic value is irreplaceable by simple model systems.”
Then title, abstract onwards everything should be re-written highlighting throughout this objective.
“The purpose of our work is not to establish a universal physical law applicable to all material systems. Rather, our goal is to establish a statistically supported structure–property relationship within a controlled compositional design space.”
The text is written with the perspective of the first sentence eventhough the objective of the latter sentence is claimed.
“The correlation between configurational entropy, oxygen octahedral distortion, Nb-O covalency and microwave properties is systematically verified from both structural and property perspectives. We believe this provides a rigorous and internally consistent evidence chain for studies on polycrystalline ceramic systems.”
A multiregression analysis to establish this point statistically is missing. With multiple number of variables, one can show almost any kind of correlation.
Fig.RR1: Without a multiregression analysis, these kind of correlations by visual comparison is meaningless.

Reviewer #3

(Remarks to the Author)
Thank you for consulting me before finalizing the decision. Having read the authors' response and Reviewer 2's latest remarks, my overall position is unchanged: I continue to support publication of this manuscript.

I want to be clear about how I read Reviewer 2's remaining concerns. In my judgment they are matters of framing and emphasis, not of data quality or scientific soundness.

The authors' multi-probe, correlation-based approach (DFT, PED, Rietveld, EXAFS, Raman, XPS) is a well-established and valuable methodology in the microwave-dielectric-ceramics community, and the underlying characterization appears rigorous and internally consistent. Reviewer 2's preference for an idealized model system is a legitimate research philosophy, but it is not the only valid one, and I do not regard the authors' choice of an application-relevant columbite system as a defect that precludes publication in this journal.

That said, I agree with Reviewer 2 on two specific points. First, the closing sentence of the abstract and several causal phrasings ("directly," "dominant cause," "complete mechanistic framework") overstate what the data establish. Through the title, abstract, and conclusions, the manuscript should consistently carry the more measured scope the authors themselves articulate, namely a structure–property relationship within a controlled compositional design space. Second, causal claims should be either supported statistically or appropriately softened. On this last point I would note, respectfully, one concern about the statistical approach. With only a handful of highly collinear compositions, a full multiple-regression analysis would carry limited statistical value. A more suitable approach would be to provide correlation and collinearity diagnostics. The mechanism could then be framed as "consistent with" the data rather than "proven." In my view, this would adequately resolve the concern.

These are bounded textual revisions that do not require new experiments. I therefore recommend acceptance subject to moderate revision along the lines above.

Version 3:

Reviewer comments:

Reviewer #3

(Remarks to the Author)
The authors addressed all my comments.

I would ask for a few minor corrections to the statistics before acceptance:

The Q×f relationship is non-monotonic. It should not be described as a "strong linear" correlation via separate segment fits. Reframe it as a peaked trend and drop the near-unity segment coefficients.
Report the sample size and p-values, and remove the excessive precision (e.g., 0.999) given the small number of compositions. Present the high VIF values as a limitation justifying the softened claims (collinearity prevents separating individual contributions), rather than as confirming evidence. Specify the regression setup in the SI.

Version 4:

Reviewer comments:

Reviewer #3

(Remarks to the Author)
The authors have carefully revised the manuscript according to my comments.

Point-by-point response

Reviewer #1

The manuscript entitled "Designable Microwave Dielectric Ceramics via Entropy-driven Oxygen Octahedral Modulation" by Jinquan Zeng et al. investigates the modulation of microwave dielectric ceramics for antenna applications through configurational entropy engineering. This approach provides an effective strategy to simultaneously optimize the key dielectric parameters (ε_r, Q×f, and τf) by collectively regulating cation displacement, octahedral distortion, and M–O bond covalency. The entropy-driven structural modulation enables synergistic property tuning and helps overcome conventional trade-offs. The optimized $NiNb_2O_6$-based medium-entropy ceramic exhibits $\varepsilon_r \approx 22.3$, Q×f ≈ 140,000 GHz, and a near-zero τ_f (−14.8 ppm/°C). Furthermore, a prototype antenna demonstrates broadband operation (5–8.5 GHz) with energy efficiency exceeding 99.98%.

The manuscript is well written and presents significant results; however, some queries and minor modifications need to be addressed before it can be considered for publication. Since the novelty of this work lies in the modulation of microwave dielectric properties through configurational entropy induced by multiple cation substitution, further clarification and discussion regarding the role, quantification, and physical implications of configurational entropy are required. In particular, the authors should clearly explain how configurational entropy is calculated, how it correlates with the degree of cation disorder, and how this disorder influences the dielectric response in the microwave frequency region. A more detailed discussion will help to better establish the structure-entropy-property relationship and strengthen the novelty and scientific rigor of the manuscript.

Response: We sincerely thank the reviewer for the positive assessment of our work and for the constructive comments on clarifying the role of configurational entropy.

In the revised manuscript, we have substantially expanded the Introduction to clarify the definition ($S_{config} = -R\Sigma x_i \ln x_i$) and physical significance of configurational entropy.

We have also clarified how configurational entropy correlates with the degree of cation disorder. In the present ANb_2O_6 system, increasing S_{config} is achieved by progressively increasing the number of A-site cation species sharing the same crystallographic site. Physically, such disorder arises from the random occupation of divalent cations with different ionic radii, electronegativities, polarizabilities, and bonding preferences, which introduces local chemical pressure, elastic strain fluctuations, and spatially inhomogeneous bonding environments. These local perturbations are transferred to the neighboring $[NbO_6]$ octahedra, which serve as the key structural units governing microwave dielectric properties, leading to broader Nb–O bond-length distributions, enhanced Nb^{5+} off-center displacement, increased octahedral distortion, and entropy-dependent Nb 4d–O 2p orbital hybridization.

We further clarified how entropy-induced cation disorder influences microwave dielectric behavior through oxygen octahedral modulation. In particular, we discuss how configurational entropy regulates three key octahedral descriptors: cation off-center displacement, octahedral distortion, and M–O bond covalency—which are closely related to ε_r, τ_f, and Q×f, respectively. These revisions establish a clearer mechanistic link between configurational entropy, local

octahedral structure, and microwave dielectric response. Additional theoretical and experimental evidence, including SQS-based DFT calculations, PDOS/ICOBI analysis, and XPS are now incorporated to support this structure–entropy–property relationship.

We believe these revisions significantly improve the clarity, scientific rigor, and novelty of the manuscript.

Detailed point-by-point responses to your comments are provided as follows:

Comment 1: The discussion on configurational entropy in the Introduction is not sufficient. The authors should elaborate on its physical significance, particularly why configurational entropy is important and how it influences dielectric behaviour and property modulation in the microwave frequency region. A clearer explanation of the underlying mechanisms linking entropy to dielectric polarization, loss, and structural dynamics would improve the scientific depth and clarity of the manuscript.

Response: We thank the reviewer for this valuable suggestion.

We have significantly expanded the discussion of configurational entropy in the Introduction to clarify its physical significance and the underlying mechanisms linking it to microwave dielectric behavior. The key revisions are summarized below:

1. Definition and physical significance of configurational entropy: We have added the formal definition: $S_{config} = -R\sum_i x_i \ln x_i$, where x_i is the molar fraction of the i^{th} element. This parameter quantifies the degree of cation disorder, providing an independent structural tuning knob distinct from conventional chemical doping. This unique capability makes configurational entropy a powerful tool for rational dielectric material design. We have incorporated this definition into the manuscript. (Page 3: lines 83-85)

2. Mechanisms linking configurational entropy to dielectric properties:

We have elaborated that configurational entropy modulates dielectric performance through its influence on oxygen octahedra—the fundamental building blocks of nearly all microwave dielectric ceramics. Specifically, it independently tunes three critical octahedral descriptors, each directly correlated with a key microwave property: (Page 3-4: lines 90-98).

(1) **Configurational entropy modulates oxygen octahedral structure and bonding**. Recent high-entropy literature has established that configurational entropy can independently affect three distinct octahedral descriptors: octahedral distortion[1-3], cation off-center displacement[4-6], and M–O bond covalency[7-9].

(2) **Octahedral characteristics directly determine microwave dielectric performance**. Each octahedral descriptor directly correlates with a specific microwave dielectric property through well-defined physical mechanisms: octahedral distortion–τ_f[10-12], M-O bond covalency–Q $\times$ f [13-15], and off-center cation displacement–ε_r[16-18].

In contrast to previous studies that focused on isolated property effects, our work establishes a complete mechanistic framework connecting configurational entropy directly to microwave performance through octahedral geometry. Based on consistent observations across ANb_2O_6, $ATiO_3$, and AAl_2O_4 systems, we propose that entropy-driven oxygen octahedral modulation represents a general and designable paradigm for high-performance microwave dielectrics.

All these revisions have been incorporated into the revised manuscript (Page 3, Lines 83–98).

Comment 2: The description of the DFT calculations in the Supplementary Information is not sufficiently clear. The authors should explicitly explain the computational methodology, particularly how the crystal structures with multiple cation species were constructed. It is unclear whether the cation distribution was modelled within a unit cell or by constructing supercells. If the calculations were performed using the crystal structure shown in Fig. 1, clarification is needed on how multiple cations were accommodated at specific lattice sites, since such disorder cannot be directly represented within a single ordered unit cell in standard DFT calculations. A detailed explanation of the structural model, cation configuration strategy (e.g., ordered approximation, supercell approach, or special quasi-random structures), and computational parameters would improve the credibility and reproducibility of the results.

Response: We thank the reviewer for this critical comment.

We have added the "**DFT Computational Details**" section in the revised Supplementary Information, providing a clear and comprehensive description of the structural models, cation configuration strategies, and computational parameters. The key revisions are summarized below:

1. Supercell construction for disordered systems

Notably, DFT calculations were not performed on the simple unit cell shown in the original Fig. 1a. Instead, we constructed 1×1×3 supercells of the orthorhombic columbite structure (space group *Pbcn*) containing 3 formula units (27 atoms total). This supercell size balances accurate representation of multi-cation disorder and computational feasibility. The crystal structure diagram in Figure 1 has been revised to show the optimized supercell obtained from our calculations.

2. A-site cation disorder modeling via Special Quasi-random Structure (SQS) method

The SQS method was adopted to model the random distribution of Ni, Mg, Zn, Co, and Mn on A-sites. This standard approach generates periodic supercells whose pair correlation functions best approximate perfectly random solid solutions. For each composition, the lowest-energy SQS configuration among the generated candidates was selected. The supercell specifications are summarized in Table R1:

Table. R1 Computational parameters for the models

Entropy	A-site composition	SQS supercell specification
Low (S=0)	Ni	Ordered (all A-sites occupied by Ni)
Low (S=0.69)	$Ni_{0.5}Mg_{0.5}$	12 A-sites: 6 Ni, 6 Mg
Medium (S=1.09R)	$Ni_{0.33}Mg_{0.33}Zn_{0.33}$	12 A-sites: 4 Ni, 4 Mg, 4 Zn
Medium (S=1.39R)	$Ni_{0.25}Mg_{0.25}Zn_{0.25}Co_{0.25}$	12 A-sites: 3 Ni, 3 Mg, 3 Zn, 3Co
High (S=1.61R)	$Ni_{0.2}Mg_{0.2}Zn_{0.2}Co_{0.2}Mn_{0.2}$	12 A-sites: 3 Ni, 3 Mg, 2 Zn, 2 Co, 2 Mn

For the five-component high-entropy composition, an exact equimolar distribution is not possible in a 12-site supercell. The closest approximation (3,3,2,2,2) yields a calculated configurational entropy of ~1.59R, which is within 2% of the ideal equimolar value (1.61R). This approximation and its justification are explicitly stated in the revised SI.

3. Computational parameters and octahedral descriptor calculation

All DFT calculations used a plane-wave basis set with an energy cutoff of 600 eV and an 8 × 16 × 8 k-point mesh for Brillouin zone sampling. Structural relaxation was converged to forces < 0.0001 eV · $Å^{-1}$ and total energy differences < 10^{-8} eV. From the optimized SQS supercells, we

extracted Nb^{5+} off-center displacement, octahedral distortion index, and Nb–O bond covalency. Detailed equations for these descriptors are provided in the revised SI.

Comment 3: In Figure 3, the authors present the evolution of M–O covalency as a function of configurational entropy using experimental techniques such as temperature-dependent Raman, EXAFS, and Nb K-edge XANES. Although these methods provide indirect evidence of O 2p–Nb 4d hybridization, more direct verification would strengthen the conclusions. The authors are encouraged to provide DFT-based electronic structure analysis, such as partial density of states (PDOS), to directly demonstrate the degree of orbital hybridization. In addition, XPS analysis could offer further experimental evidence of the covalent character and would complement the interpretation of the entropy-driven covalency modulation.

Response: We thank the reviewer for this constructive suggestion.

In response, we have performed three additional sets of analyses as requested and incorporated them into the revised manuscript: DFT-calculated partial density of states (PDOS) for direct visualization of orbital hybridization, DFT-calculated Integrated Crystal Orbital Bond Index (ICOBI) for quantitative covalency measurement, and X-ray photoelectron spectroscopy (XPS) for experimental validation. All results consistently confirm the non-monotonic entropy dependence of Nb–O covalency, which peaks at medium entropy.

1. DFT PDOS analysis

PDOS calculations for Nb 4d and O 2p states were performed using the established SQS supercell models. Figure R1 shows the PDOS of all five compositions, revealing that the spectral overlap between Nb 4d and O 2p orbitals increases by 27% at medium entropy compared to the low-entropy endmember, then decreases at high entropy. These results provide **visual confirmation of entropy-driven changes in Nb 4d-O 2p orbital hybridization**.

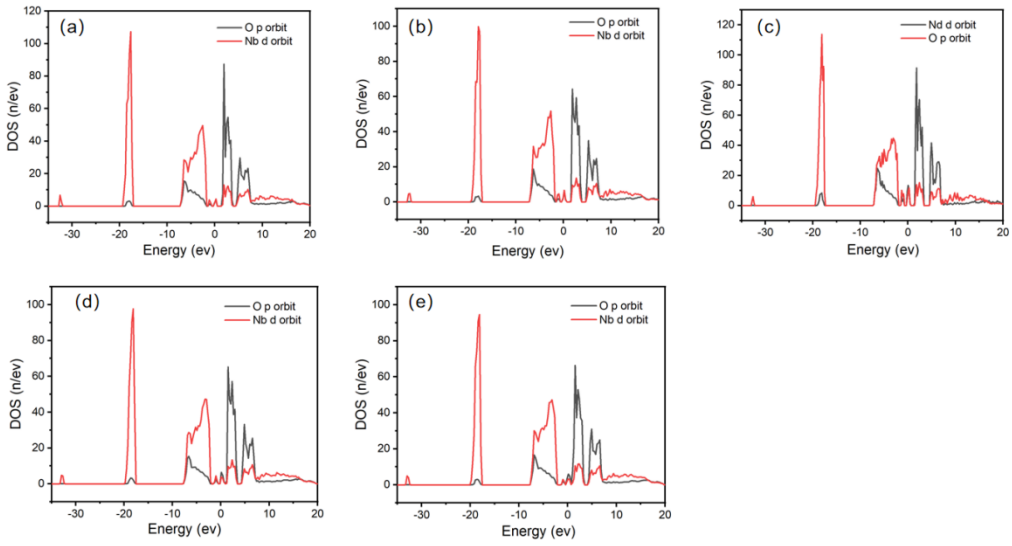

Fig. R1 The PDOS of (a) $NiNb_2O_6$ (b) $(Ni,Mg)_{0.5}Nb_2O_6$ (c) $(Ni,Mg,Zn)_{1/3}Nb_2O_6$ (d) $(Ni,Mg,Zn,Co)_{0.25}Nb_2O_6$ (e) $(Ni,Mg,Zn,Co,Mn)_{0.2}Nb_2O_6$

2. DFT ICOBI analysis

We further calculated the integrated crystal orbital bond index (ICOBI) to quantify Nb-O covalency variations. As shown in Figure R2, the ICOBI value peaks at 0.824 for the

medium-entropy composition and decreases to 0.803 for the high-entropy composition, quantitatively **validating the non-monotonic covalency trend**.

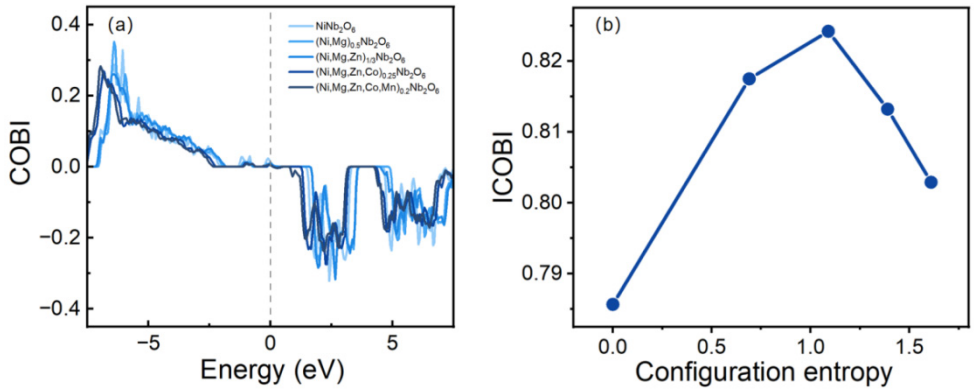

Figure. R2 (a) the COBI around -8 to 8 ev and (b) ICOBI values for Nb–O bonds across low-, medium-, and high-entropy compositions.

3. XPS experimental validation

XPS measurements were conducted to experimentally verify the covalency trend. Stronger Nb–O covalency reduces the binding energy of the Nb $3d_{5/2}$ core level due to enhanced electron screening. As displayed in Figure R3, the medium-entropy sample shows the lowest Nb $3d_{5/2}$ binding energy (206.6 eV), consistent with its maximum covalency. The binding energy increases to 206.8 eV for the low-entropy composition and 206.9 eV for the high-entropy counterpart, fully reproducing the theoretical trend.

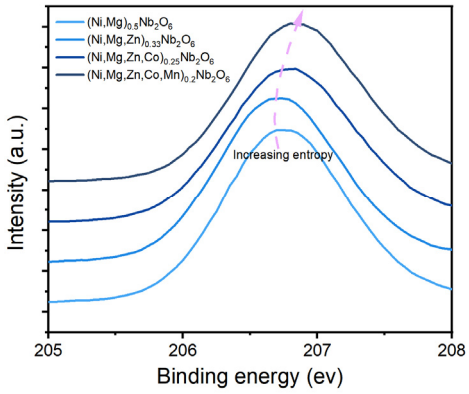

Figure. R3 The Nb $3d_{5/2}$ peak of XPS spectra

All new results have been added as Figure S6 in the Supporting Information, with corresponding discussion included in the manuscript (Page 8, Lines 239–242).

Reviewer #2:

This is an interesting effort to arrive at a means to achieve a difficult set of combination of parameters to make a material suitable for microwave dielectric resonators, namely high dielectric loss, low loss and low value of temperature coefficient of resonant frequency.

Response: We sincerely thank the reviewer for the interest of our work. We agree that the simultaneous realization of high permittivity, low dielectric loss, and a near-zero temperature coefficient of resonant frequency is a key challenge for microwave dielectric resonator materials. In the revised manuscript, we have clarified that the significance of this work lies not only in achieving a balanced set of microwave dielectric properties, but also in establishing configurational entropy engineering as a general and designable strategy for regulating oxygen-octahedral structure and synergistically tuning ε_r, Q×f, and τ_f. We have also cited the benchmark $Ba(Mg_{1/3}Ta_{2/3})O_3$ and expanded the analysis of both intrinsic and extrinsic factors in response to the reviewer's comments.

Detailed point-by-point responses to your comments are provided as follows:

Comment 1: But the authors achieved a set of values as ϵ' ~22.3, Q×f (~140000 GHz), and τ_f (-14.8 ppm/°C) in $NiNb_2O_6$. However it is far less impressive the dielectric resonator available in the dielectric constant range around 25. Nomura, S., Toyama, K., & Kaneta, K. (1982). "$Ba(Mg_{1/3}Ta_{2/3})O_3$ Ceramics with Temperature-Stable High Dielectric Constant and Low Microwave Loss." Japanese Journal of Applied Physics, 21(10), L624. They report the following set of parameters in 1982 itself:

Dielectric Constant:25

Quality Factor : 17,600 (at 10 GHz), Q.f 176,000 GHz

Temperature Coeff: 4 ppm/°C

Later other workers reduced the τf of this composition to ~0 to 0.5 ppm/°C (Peng et al., 2023).

Therefore, after nearly half a century, what is claimed by the present authors as a great combination of results is not so.

Response: We thank the reviewer for this important comment and for bringing these classic and recent benchmark works to our attention.

We fully acknowledge that $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) represents a state-of-the-art benchmark for microwave dielectrics, with exceptional performance (ε_r ~25, Q×f ~176,000 GHz, τ_f ~4 ppm/°C) first reported in 1982 and further optimized to near-zero τ_f in subsequent studies (Peng *et al.*, 2023). Their contributions are now cited as ***Refs. 69* and *70***. This entropy-driven approach yields balanced performance in a medium-entropy composition (ε_r ~ 22.3, Q×f ~ 140,000 GHz, τ_f = -14.8 ppm/°C), which is competitive within the ε_r ~22 class and complements existing high-performance materials such as $Ba(Mg_{1/3}Ta_{2/3})O_3$. However, BMT suffers from two critical practical limitations that have restricted its widespread industrial application: a **high sintering temperature (>1600 °C)** and reliance **on high-cost Ta-containing** raw materials. Such limitations remain unresolved even with recent τ_f optimizations.

Compared to the widely used commercial K21 (*i.e.* $MgTiO_3$-$CaTiO_3$) dielectrics, our medium-entropy composition exhibits a higher relative permittivity (ε_r ~22.3 vs. ~21) and

comparable temperature coefficient of resonant frequency (τ_f ~ -14.8 ppm/°C vs. ~0-10 ppm/°C), while delivering a much higher Q×f (~140,000 GHz vs. ~50,000-80,000 GHz) as well as a lower sintering temperature (1150-1300 °C vs. 1300-1400 °C).

More broadly, our work is not merely to report a single high-performance composition, but to establish a general and designable materials paradigm: configurational entropy engineering as a unified lever to synergistically tune all three key microwave dielectric parameters (ε_r, Q×f, τ_f) through modulation of oxygen octahedral geometry. This strategy is also effective in the $ATiO_3$ and AAl_2O_4 systems.

Comment 2: A DRA is fabricated for demonstrating the superiority with this composition. However any dielectric resonator with these set of material parameters will give the same response with the chosen design. It has nothing to with the composition.

Response: We appreciate the reviewer's comment.

We acknowledge that materials with identical intrinsic dielectric parameters and device dimensions will yield similar resonant performance in theory. However, practical DRA implementation critically depends on material processing characteristics that are inherently determined by composition, such as **machinability, sintering behavior, microstructure stability, and interfacial compatibility with device components**.

As a reference, BMT ceramics possess excellent intrinsic microwave properties but suffer from high hardness, narrow sintering window, and poor machinability, which have limited their widespread practical application[19,20]. In contrast, our medium-entropy ceramic features a wide sintering window, moderate hardness, uniform microstructure, reliable machinability, and good adhesion with standard device materials. These composition-dependent merits enabled the successful fabrication of high-performance DRA prototypes.

This DRA demonstration bridges fundamental material research and practical device applications, verifying the application potential of our developed ceramic. The above points have been clarified in the revised manuscript (Page 11 Lines 315-317).

Comment 3: "As shown in Fig. 4a, the ε_r increases monotonically with configurational entropy, rising from 21.6 in low-entropy compositions to 23.3 in the high-entropy variant." The compositions vary widely to achieve variation in configurational entropy. That will result in different sinterability and resulting in differences in final densities, grain size, grain boundaries etc for the resulting compositions. The narrow range of dielectric constant variation can easily because of these extraneous factors. It is very difficult to correlate these small changes to intrinsic factors like changes in configurational entropy. In ensembles where the variation is so large that the variations can be solely attributed to intrinsic factors, the proposed hypothesis can be tested.

Response: We thank the reviewer for this critical and insightful comment. We fully agree that extrinsic factors such as sinterability, density, and grain size can influence dielectric properties, and we have performed systematic control experiments to decouple these effects from intrinsic entropy-driven contributions. The following evidence confirms that the observed monotonic increase in ε_r is primarily intrinsic in origin:

1. **Sinterability and density control**

For each composition, we optimized sintering temperature to achieve >95% relative density. The optimal sintering temperature decreases slightly with increasing entropy (1225 °C for

low-entropy, 1175 °C for high-entropy) due to enhanced sinterability from multi-element mixing. Critically, the monotonic ε_r increase with entropy is preserved across all tested sintering temperatures (1150–1300 °C), even at sub-optimal temperatures where densities are slightly lower. This demonstrates that the trend is not an artifact of density differences.

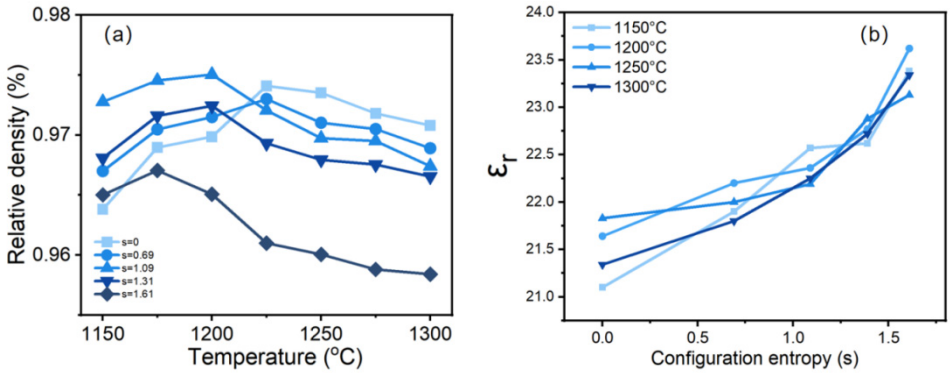

Figure. R4 (a) The relative density from 1150 to 1300°C and (b) ε_r from 1150 to 1300°C

2. **Grain size analysis**

SEM characterization shows that average grain size decreases monotonically with increasing configurational entropy, a well-known effect of sluggish diffusion in high-entropy ceramics. If grain size were the dominant factor, ε_r would be expected to decrease with decreasing grain size (due to increased low-permittivity grain boundary layer). The observed opposite trend rules out grain size as the primary cause of the ε_r variation.

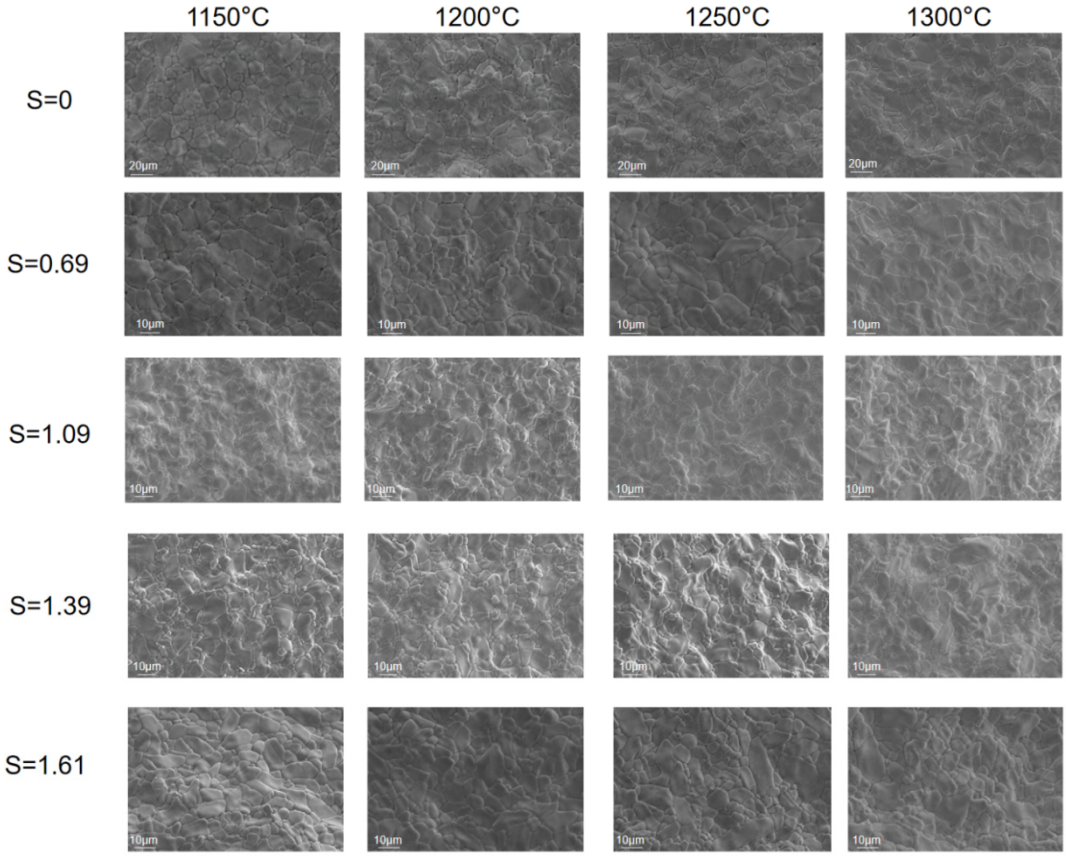

Figure. R5 SEM images of S=0, 0.69, 1.09, 1.39 and 1.61 from 1150 to 1300°C

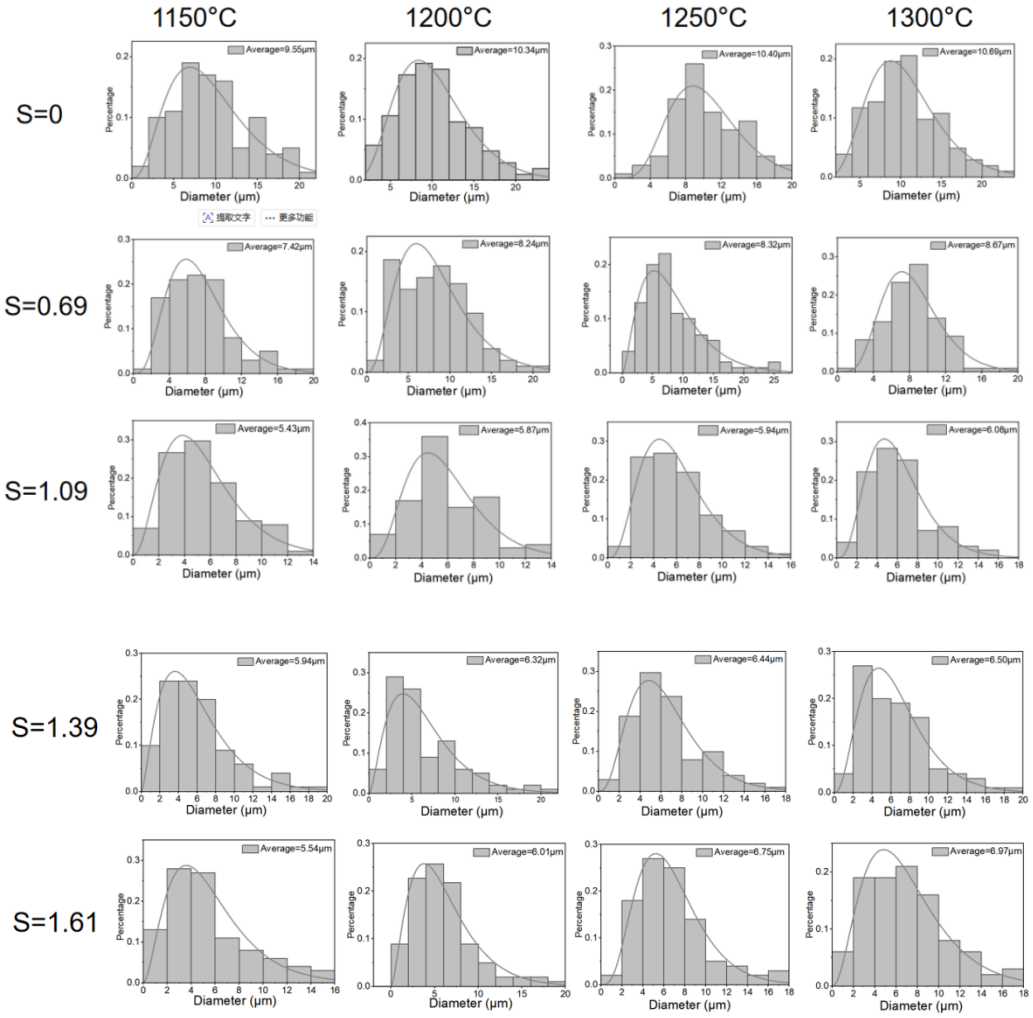

Figure. R6 Grain size distributions of S=0, 0.69, 1.09, 1.39 and 1.61 from 1150 to 1300°C

Therefore, while grain size may have a secondary contribution, the dominant factor governing the microwave dielectric properties in this study is the intrinsic effect of configurational entropy. A brief discussion has been added in the revised Manuscript (Page 10, Lines 272-277).

3. Residual porosity correction

We applied the Lichtenecker logarithmic mixing rule to correct measured ε_r values for residual porosity. As shown in Table R2, the porosity-corrected ε_r values retain the identical monotonic entropy trend as the raw data, confirming that porosity is not the origin of the observed variation.

Table. R2 ε_r considering porosity

Composition	S_{config} (R)	ρ_{rel}	P (optical)	ε_{exp}	ε_{corr}
$NiNb_2O_6$	0	0.974	0.026	21.7	22.3
$(Ni,Mg)_{0.5}Nb_2O_6$	0.69	0.973	0.027	21.9	22.5
$(Ni,Mg,Zn)_{1/3}Nb_2O_6$	1.09	0.975	0.025	22.1	22.7
$(Ni,Mg,Zn,Co)_{0.25}Nb_2O_6$	1.39	0.972	0.028	22.4	23.0
$(Ni,Mg,Zn,Co,Mn)_{0.2}Nb_2O_6$	1.61	0.967	0.033	23.3	24.1

All major extrinsic factors have been systematically excluded. The observed ε_r increase from 21.6 to 23.3 is therefore attributed to intrinsic configurational entropy-driven structural changes. Relevant discussion has been added to the revised manuscript (Page 10, Lines 277–281).

Comment 4: "Q×f exhibits non-monotonic behavior, peaking at ~140,000 GHz in the medium-entropy composition before declining at higher entropy (Figs. 4c). This mirrors the covalency maximum observed by calculation prediction and covalency validations, indicating that optimal Nb-O orbital hybridization at intermediate entropy minimizes intrinsic dielectric loss by suppressing anharmonic phonon scattering." The loss factor is quite sensitive to both intrinsic and extrinsic factors which are well studied by Kamba et al. In each of the compositions considered in the Fig.4c, the reason for the variation in Q value could be quite different. It is known that increased covalency will lock up the ions to minimize the lattice vibration based intrinsic loss. Since a wide range of intrinsic and extrinsic parameters are responsible for the variation of Q factor, attributing the observed variation solely to the configurational entropy is questionable.

Response: We sincerely thank the reviewer for highlighting the important point that increased covalency can lock up the ions and thereby minimize lattice-vibration-based intrinsic loss. Accordingly, we have added a discussion in the revised manuscript (Page 10, Lines 287–290).

We fully agree that Q×f is sensitive to both intrinsic and extrinsic factors, as comprehensively established by Kamba et al. (now properly cited in the revised manuscript, ***Ref. 41***). We agree that configurational entropy is not the only factor governing Q×f. Instead, we have systematically eliminated all major confounding variables through rigorous control experiments, demonstrating that **entropy-modulated Nb–O covalency is the dominant origin of the observed non-monotonic Q×f trend**.

On one hand, we designed experiments to study the aforementioned extrinsic factors. All compositions achieve ＞95% relative density (Fig.R4). SEM analysis revealed that grain size decreases monotonically with increasing entropy (Fig.R5, R6). If grain size were dominant, Q×f would be expected to decrease monotonically with decreasing grain size (since more grain boundaries introduce more scattering). The observed non-monotonic Q×f, peaking at medium entropy and declining despite further grain size reduction, contradicts this expectation, ruling out grain size as the primary factor. The porosity-corrected Q×f values show the same non-monotonic entropy trend as the raw data in Table.R4. XRD confirms single-phase columbite for all compositions (＞99%), eliminating secondary phase formation as a contributor to Q×f variations. O 1s XPS spectra show that the oxygen-vacancy concentration slightly increases with increasing entropy (Fig. R7). Overall, it remains stable with no significant fluctuations. **On the other hand**, we extended our investigation to multiple material systems beyond the ANb_2O_6 to $ATiO_3$ and spinel AAl_2O_4 systems. Across these distinct systems, we observed a consistent, non-monotonic relationship between configurational entropy and Q×f, with the peak consistently appearing at medium-entropy compositions. This universality strongly suggests that the observed trend is not a fortuitous result of extrinsic variations. We do not claim configurational entropy is the only factor governing Q×f. Instead, our control experiments have eliminated all major confounding variables, indicating that entropy-modulated Nb-O covalency is the dominant cause of the non-monotonic Q×f trend.

Table. R3 External influencing factors

Factor	Control measure	Finding
Relative density	Sintering temperature (1150–1300 °C)	All compositions ≥95%; Corrected Q×f shows same non-monotonic trend
Porosity	Lichtenecker porosity correction applied	
Grain size	SEM analysis	The grain size slightly decreases as the entropy increases
Secondary phases	XRD	Single-phase columbite for all compositions

Table. R4 Q×f considering porosity

Compostition	S (R)	$Q \times f_{exp}$ (GHz)	ρ_{rel}	p	$Q \times f_{corr}$ (GHz)
Ni	0	32,048	0.974	0.026	32,882
(Ni,Mg)	0.69	99,430	0.973	0.027	102,210
(Ni,Mg,Zn)	1.09	140,650	0.975	0.025	143,887
(Ni,Mg,Zn,Co)	1.39	75,787	0.972	0.028	78,051
(Ni,Mg,Zn,Co,Mn)	1.61	18,043	0.967	0.033	18,647

Relevant discussion on the multi-factor nature of Q×f has been added to the revised manuscript (Page 10, Lines 272–277).

Comment 5: "τ_f shifts toward more positive values with increasing entropy, as depicted in Figs. 4b. This improvement arises from entropy-induced octahedral distortion, which strengthens the restoring force for temperature-dependent tilting modes of the [NbO_6] framework, thereby stabilizing resonance against thermal fluctuations." In this case also for each composition, the origin of the τ_f depends on cancelling the effect of thermal expansion with the effect of permittivity variation with temperature. Multiple factors are involved and simply attributing the observed changes only to configurational entropy is not justified. First of all, such small changes need not be completely intrinsic in origin. We are dealing with ceramics which are sintered at high temperature. They are bound to have oxygen vacancies. Without considering all the associated factors, we can not attribute the entire changes to configurational entropy.

Response: The authors thank the reviewer for this valuable comment.

We thank the reviewer for this valuable comment. We fully agree that τ_f is determined by the balance between the temperature coefficient of permittivity (τ_ε) and the linear thermal expansion coefficient (αL), and is influenced by multiple intrinsic and extrinsic factors. We do not claim configurational entropy is the sole factor governing τ_f. Instead, we have systematically excluded all major extrinsic confounding variables, demonstrating that entropy-induced [NbO_6] octahedral

distortion is the dominant origin of the observed monotonic τ_f shift. All major extrinsic factors have been ruled out as the primary cause:

Density, porosity and secondary phases: All compositions achieve >95% relative density, <5% residual porosity, and >99% phase-pure columbite structure, eliminating these factors as significant contributors to τ_f variation.

Oxygen vacancies: Our XPS O 1s characterization indicates that the oxygen vacancy concentration shows a moderate increase from 18.3% to 25.1% with increasing configurational entropy (Table R5). If oxygen vacancies played a dominant role in determining τ_f, we would anticipate a monotonic negative shift of τ_f, consistent with the lattice softening effect associated with oxygen vacancies as documented in prior studies. In contrast, the experimentally observed τ_f evolution matches well with the trend of entropy-induced octahedral distortion measured independently via EXAFS and Raman spectroscopy, but does not correlate with the change in oxygen vacancy concentration. This observed decoupling suggests that oxygen vacancies are unlikely to be the primary cause of the τ_f variation reported in this work. Our combined EXAFS and Raman measurements consistently show that configurational entropy modulates the extent of $[NbO_6]$ octahedral distortion, which directly affects both τ_ε and αL—the two fundamental parameters that contribute to τ_f. This intrinsic structural effect provides a coherent explanation for the observed monotonic shift of τ_f to more positive values as configurational entropy increases.

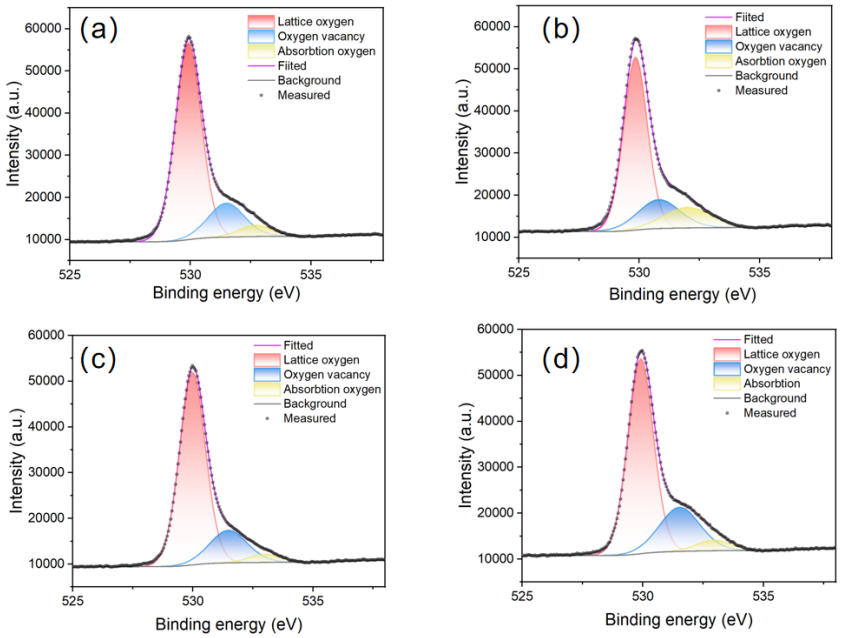

Figure. R7 O 1s XPS spectra of (a) $(Ni,Mg)_{0.5}Nb_2O_6$ (b) $(Ni,Mg,Zn)_{1/3}Nb_2O_6$ (c) $(Ni,Mg,Zn,Co)_{0.25}Nb_2O_6$ (d) $(Ni,Mg,Zn,Co,Mn)_{0.2}Nb_2O_6$

Table. R5 Oxygen vacancy content

Composition	V_O (%)
$(Ni,Mg)_{0.5}Nb_2O_6$	18.3
$(Ni,Mg,Zn)_{1/3}Nb_2O_6$	19.7
$(Ni,Mg,Zn,Co)_{0.25}Nb_2O_6$	21.2
$(Ni,Mg,Zn,Co,Mn)_{0.2}Nb_2O_6$	25.1

Relevant discussion on the multi-factor nature of τ_f and the role of octahedral distortion has been added to the revised manuscript (Page 10, Lines 282–285).

Comment 6: However configurational entropy is a key parameter and it can guide material engineering, if the influence of each parameters are carefully understood and controlled. It is better done in systems where extrinsic factors are few and their role across composition variation are predictable. In a sintered ceramic system, subtle intrinsic factors get greatly submerged by a wide variety of extrinsic factors which act differently with changes in composition.

Response: We thank the reviewer for this thoughtful and insightful summary comment. We fully agree with your profound observation that while configurational entropy holds great promise for guiding materials engineering, its influence must be carefully disentangled from extrinsic factors, especially in sintered ceramic systems where subtle intrinsic effects can be easily masked by a variety of extrinsic contributions that vary with composition. To address this critical challenge, we have performed a comprehensive set of control experiments to systematically isolate intrinsic entropy-driven effects from extrinsic contributions:

1. **Sintering temperature optimization (1150–1300 °C):** All compositions achieve ≥95% relative density.
2. **Grain size analysis:** SEM characterization confirmed that grain size decreases monotonically with increasing entropy, and we have demonstrated that this trend cannot explain the observed dielectric property variations.
3. **Porosity correction:** The porosity-corrected microwave dielectric properties retain the identical entropy-dependent trends as the raw data.
4. **Oxygen vacancy quantification:** XPS O 1s analysis shows oxygen vacancy concentration increases moderately from 18.3% to 25.1% with entropy, and we have ruled out vacancies as the primary cause of the observed property changes.

We have incorporated this important viewpoint into the revised manuscript (Lines 272–292). **Our future work will focus on more precise quantification and control of extrinsic influences such as porosity, grain boundaries, and oxygen vacancies to further advance the entropy engineering paradigm for high-performance microwave dielectric ceramics.**

We greatly appreciate all your constructive comments, which have significantly improved the rigor and clarity of our manuscript.

Reviewer #3

In this work, ANb_2O_6-based ceramics were developed to achieve an optimized relative dielectric constant, ultra-low dielectric loss, and a near-zero temperature coefficient of resonant frequency. The authors introduced configurational entropy as a global index to simultaneously regulate cation displacement, octahedral distortion, and M-O bond covalency, effectively bypassing the intrinsic trade-offs that typically hinder the independent optimization of microwave dielectric parameters. This strategy enabled the fabrication of a prototype dielectric antenna that outperforms state-of-the-art devices. The research topic is significant, the entropy-driven design approach is innovative, and the experimental data are robust. This manuscript meets the scope and standards of Nature Communications and is recommended for publication after the following minor issues are addressed:

We sincerely thank the reviewer for the encouraging and positive assessment of our manuscript.

We also appreciate the reviewer's careful reading of the manuscript and the constructive suggestions for further improvement. We have addressed all the minor issues raised by the reviewer point by point and revised the manuscript accordingly. We believe that these revisions have further improved the clarity and quality of the manuscript.

Detailed point-by-point responses to your comments are provided as follows:

Comment 1: In the introduction, are there other high-entropy microwave dielectric studies that should be cited to position the present contribution more precisely? Additionally, the connection between configurational entropy and octahedral decoupling would benefit from a bridging statement. The authors explain that entropy expands solubility and preserves single-phase integrity but do not explicitly clarify why this should decouple the $\varepsilon_r/Q\times f/\tau_f$ trade-offs.

Response: We thank the reviewer for these valuable suggestions. We have revised the Introduction to address both points as follows:

1, Literature supplementation and contribution positioning

We have added citations to several representative recent studies on high-entropy microwave dielectric ceramics (Page 4, Lines 90–96) to more precisely position our contribution within the existing literature. These studies confirm that configurational entropy can independently modulate three critical octahedral descriptors: octahedral distortion[1-3], cation off-center displacement[4-6], and M–O bond covalency[7-9]. Each descriptor directly correlates with a key microwave dielectric property through well-established physical mechanisms: octahedral distortion determines τ_f[10-12], M–O bond covalency governs $Q\times f$[13-15], and cation off-center displacement controls ε_r[16-18].

2, Bridging statement for entropy-driven trade-off decoupling

We have added an explicit bridging statement to explain how configurational entropy breaks the classic $\varepsilon_r/Q\times f/\tau_f$ trade-off (Page 4, Lines 90–98). Traditional chemical doping strategies are limited by narrow solubility windows and inevitable secondary phase formation, which typically alter multiple octahedral parameters simultaneously, making independent tuning of the three dielectric properties impossible. In contrast, high configurational entropy significantly expands the single-phase stability window, allowing continuous modulation of the octahedral framework over a broad compositional range. Critically, the three octahedral descriptors exhibit distinct and differential responses to increasing configurational entropy. This unique characteristic enables

quasi-independent tuning of ε_r, $Q\times f$, and τ_f, thereby breaking the conventional performance trade-off.

Comment 2: In the experimental procedure section, it would be helpful to specify the elemental composition for each sample (e.g., $Ni_{0.5}Mg_{0.5}$, $Ni_{0.2}Mg_{0.2}Zn_{0.2}Co_{0.2}Mn_{0.2}$, etc.) to avoid ambiguity. Additionally, only four compositions appear to be presented. Is there a missing composition, specifically the one with s=1.39?

Response: We thank the reviewer for this helpful suggestion.

We have revised the sample compositions and added $(Ni,Mg,Zn,Co)_{0.25}$ in the experimental procedure section. All five compositions are present in the manuscript. Configurational entropy was calculated using the formula: $S_{config}= -R\Sigma x_i \ln x_i$, where x_i is the molar fraction of each A-site cation.

Table. R6 Configurational entropy for each composition

Sample	Chemical formula	$S_{config}(R)$
S=0	$NiNb_2O_6$	0
S=0.69	$(Ni，Mg)_{0.5}Nb_2O_6$	0.69
S=1.09	$(Ni,Mg,Zn)_{0.33}Nb_2O_6$	1.09
S=1.39	$(Ni,Mg,Zn,Co)_{0.25}Nb_2O_6$	1.39
S=1.61	$(Ni,Mg,Zn,Co,Mn)_{0.2}Nb_2O_6$	1.61

All revisions have been incorporated into the revised manuscript, Experimental Procedure section.

Comment 3: The term "medium-entropy" is used throughout the manuscript without a precise definition. The boundaries between low-, medium-, and high-entropy classifications should be explicitly defined (e.g., S < 1R as low, 1R-1.5R as medium, and >1.5R as high). Do the authors follow this convention or an alternative one?

Response: We thank the reviewer for this important clarification. We have explicitly defined the entropy classification boundaries in the revised manuscript in experimental procedure section, following the widely accepted convention established by Rost et al. (Nat. Commun. 2015, 6, 8485) for high-entropy oxides: $S_{config}= -R\Sigma x_i \ln x_i$, where x_i is the molar fraction of each A-site cation.

Table. R7 Classification boundaries of configurational entropy

Entropy	Classification	Description
$S < 1R$	Low entropy	Single-principal-element or dilute doping compositions
$1R \leq S < 1.5R$	Medium entropy	Multi-principal-element compositions with moderate configurational disorder
$S \geq 1.5R$	High entropy	Compositions with five or more equimolar principal elements

Based on this classification, our five compositions are categorized as follows:

Table. R8 Classification of each composition

A-site composition	S_{config}(R)	Classification
Ni	0	Low entropy
$(Ni,Mg)_{0.5}$	0.69	Low entropy (S < 1R)
$(Ni,Mg,Zn)_{1/3}$	1.09	Medium entropy (1R ≤ S < 1.5R)
$(Ni,Mg,Zn,Co)_{0.25}$	1.39	Medium entropy (1R ≤ S < 1.5R)
$(Ni,Mg,Zn,Co,Mn)_{0.2}$	1.61	High entropy (S ≥ 1.5R)

Comment 4: Figures 1a and 1b appear to be swapped. Please verify that the figure labels are consistent with the corresponding descriptions in the text and captions.

Response: We thank the reviewer for carefully checking our figures. We have verified that the labels of Fig. 1a and 1b were correct in the original submission, but the corresponding description sequence in the main text was out of order. This discrepancy has been corrected in the revised manuscript. Additionally, we have comprehensively redesigned Fig. 1 to address other reviewer comments and improve clarity. All figure labels and text descriptions are now fully consistent.

Comment 5: The sintering temperature range is reported as 1150-1300°C, but the specific optimal sintering temperature for each composition is not stated. Given that different A-site compositions are likely to have different optimal sintering windows, this information is important for reproducibility.

Response: We thank the reviewer for this important comment regarding reproducibility. We have systematically investigated the sintering behavior of all five compositions and added their optimal sintering temperatures to the revised supporting information, Table S2.
The optimal sintering temperature for each composition is summarized below:

Table. R9 The optimal sintering temperature

Composition	S_{config} (R)	Optimal sintering temperature (±15°C)
$NiNb_2O_6$	0	1225 °C
$(Ni,Mg)_{0.5}Nb_2O_6$	0.69	1225 °C
$(Ni,Mg,Zn)_{1/3}Nb_2O_6$	1.09	1200 °C
$(Ni,Mg,Zn,Co)_{0.25}Nb_2O_6$	1.39	1200 °C
$(Ni,Mg,Zn,Co,Mn)_{0.2}Nb_2O_6$	1.61	1175 °C

All reported microwave dielectric properties correspond to samples sintered at these optimal temperatures.

Comment 6: The non-monotonic covalency trend is among the most novel findings in this work; however, the physical explanation remains somewhat unclear. Why does covalency peak at medium entropy and then decrease? The authors attribute this behavior to changes in orbital hybridization, but a clearer mechanistic explanation would strengthen the discussion. For example, is this trend related to competing local distortion effects or to the specific electronic configurations of Co^{2+} and Mn^{2+} introduced at higher entropy levels?

Response: We thank the reviewer for highlighting this important point. We agree that the non-monotonic covalency trend is a key finding, and a clearer mechanistic explanation is warranted. Below we provide a detailed physical explanation based on our DFT calculations and experimental observations. The non-monotonic Nb–O covalency trend arises from the nonlinear relationship between entropy-induced local lattice distortion and orbital overlap:

Low to medium entropy (moderate distortion): Increasing configurational entropy introduces A-site cation disorder, generating local chemical pressure that breaks lattice symmetry and enhances Nb 4d–O 2p orbital overlap, thereby increasing covalency. This is consistent with well-documented chemical pressure effects in oxide systems[21].

Medium to high entropy (excessive distortion): Further increases in entropy introduce cations with more diverse ionic radii, leading to accumulated local strain and over-distortion of [NbO_6] octahedra. This misaligns Nb and O orbitals, reducing orbital overlap and decreasing covalency. Covalency is thus maximized at an intermediate distortion level—sufficient to activate orbital hybridization but not severe enough to disrupt orbital alignment.

To confirm that this trend is governed by local distortion rather than the specific electronic configurations of Co^{2+} and Mn^{2+}, we performed **control experiments on Mn-based columbite ceramics with identical entropy levels**. The compositions ($MnNb_2O6$, $(Mn,Mg)_{0.5}Nb_2O_6$, $(Mn,Mg,Zn)_{1/3}Nb_2O_6$, $(Mn,Mg,Zn,Co)_{0.25}Nb_2O_6$, $(Ni,Mg,Zn,Co,Mn)_{0.2}Nb_2O_6$) are in the same entropy levels (S = 0, 0.69, 1.09, 1.39, 1.61R). The same non-monotonic covalency trend was observed in the Mn-based system, demonstrating that this is a general phenomenon driven by entropy-induced lattice distortion, independent of specific cation identities.

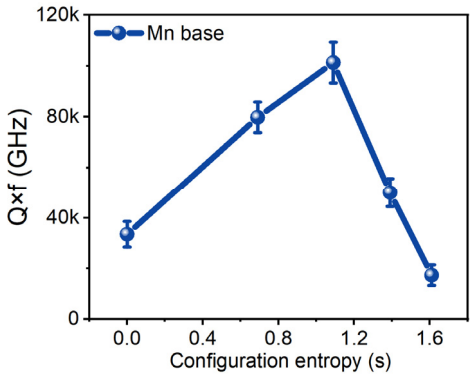

Figure. R8 Q×f of Mn-base configurational entropy control compositions of $MnNb_2O_6$, $(Mn,Mg)_{0.5}Nb_2O_6$, $(Mn,Mg,Zn)_{1/3}Nb_2O_6$, $(Mn,Mg,Zn,Co)_{0.25}Nb_2O_6$, and $(Ni,Mg,Zn,Co,Mn)_{0.2}Nb_2O_6$

This discussion has been added to the main manuscript (Page 9, Lines 258–261, and Page 10, Lines 290–292).

Comment 6: The precession electron diffraction (PED)-derived pair distribution functon (PDF) analysis is used to validate DFT predictions of Nb-O bond length changes. However, the manuscript does not discuss the uncertainty or resolution limits of PED-based PDF for distinguishing sub-0.1 Å differences in bond length. A brief discussion of the precision of this technique in this context would strengthen the validity of the claim.

Response: We thank the reviewer for this important methodological question. We have added a brief discussion of the precision of PED-based electron pair distribution function (ePDF) analysis in the revised manuscript to validate our bond length measurements.

PED minimizes multiple scattering effects and exhibits quasi-kinematical diffraction characteristics, enabling quantitative local structural analysis with an interatomic distance precision of 0.01–0.03 Å[22-24]. This precision is sufficient to reliably distinguish bond length differences well below 0.1 Å, and the accuracy of PED-ePDF is comparable to synchrotron-based PDF methods.

In our study, the measured Nb–O bond length variations across the compositional series range from 0.05 Å to 0.08 Å, which are significantly larger than the intrinsic measurement uncertainty. This confirms that the observed bond length changes are statistically significant and consistent with our DFT predictions.

This discussion has been added to the main manuscript (Page 8, Lines 216–219).

Comment 7: What are the A-site elements in $ATiO_3$ and AAl_2O_4? Are they the same elements used in the ANb_2O_6 system?

Response: We thank the reviewer for this clarification question.

The A-site cations adopted in $ATiO_3$ and AAl_2O_4 are identical to those in the ANb_2O_6 system. As summarized in Table R10, five A-site compositions with graded configurational entropy were applied to all three material families: ANb_2O_6, $ATiO_3$ and AAl_2O_4. The B-site cations differ across systems Nb^{5+}, Ti^{4+}, Al^{3+}, while the A-site component and entropy levels remain unchanged. This unified design enables us to decouple the influence of structural type and B-site ions, and verifies the general applicability of the entropy-driven modulation strategy across diverse octahedral-based ceramics. We have supplemented the above clarification in the Experimental section of the revised manuscript.

Table. R10 Summary of A site cations

A-site composition	Number of cations	S_{config} (R)
Ni	1	0
$Ni_{0.5}Mg_{0.5}$	2	0.69
$Ni_{1/3}Mg_{1/3}Zn_{1/3}$	3	1.09
$Ni_{0.25}Mg_{0.25}Zn_{0.25}Co_{0.25}$	4	1.39
$Ni_{0.2}Mg_{0.2}Zn_{0.2}Co_{0.2}Mn_{0.2}$	5	1.61

This clarification has been added to the Experimental section of the revised manuscript.

Comment 8: There are typographical errors in the references. For example, "Cream." should be corrected to "Ceram." for ceramics-related journal titles.

Response: We thank the reviewer for carefully checking our references. We have thoroughly reviewed and corrected all references in the revised manuscript.

We are grateful for your insightful advice that facilitates upgrading the manuscript and clarifying our descriptions. We have fully implemented relevant revisions and respectfully request consideration for publication.

Reference

1 Zou, G. *et al.* High-entropy-induced CoO_6 octahedral distortion for boosted oxygen evolution reaction at high temperature. *Energy Environ. Sci.* **18**, 9478–9489 (2025). https://doi.org/10.1039/d5ee01370d

2 Bakradze, G., Welter, E. & Kuzmin, A. Peculiarities of the local structure in new medium- and high-entropy, low-symmetry tungstates. *J. Phys. Chem. Solids* **172** (2023). https://doi.org/10.1016/j.jpcs.2022.111052

3 Zhang, M. *et al.* Ultrahigh energy storage in high-entropy ceramic capacitors with polymorphic relaxor phase. *Science* **384**, 185–189 (2024). https://doi.org/10.1126/science.adl2931

4 Yang, B. *et al.* Engineering relaxors by entropy for high energy storage performance. *Nat. Energy* **8**, 956–964 (2023). https://doi.org/10.1038/s41560-023-01300-0

5 Duan, J. *et al.* High-entropy superparaelectrics with locally diverse ferroic distortion for high-capacitive energy storage. *Nat. Commun.* **15** (2024). https://doi.org/10.1038/s41467-024-51058-6

6 Zhou, S. *et al.* Ultrawide-temperature-stable high-entropy relaxor ferroelectrics for energy-efficient capacitors. *Nat. Commun.* **16** (2025). https://doi.org/10.1038/s41467-025-63173-z

7 Su, L. *et al.* Direct observation of elemental fluctuation and oxygen octahedral distortion-dependent charge distribution in high entropy oxides. *Nat. Commun.* **13** (2022). https://doi.org/10.1038/s41467-022-30018-y

8 Wang, J. *et al.* Modulating metal-oxygen interactions of high-entropy oxide electrocatalysts enables highly-active and ultra-stable water oxidation. *Appl. Catal. B Environ. Energy* **342** (2024). https://doi.org/10.1016/j.apcatb.2023.123382

9 Gayathri, S. *et al.* Modulating Coordination-Driven Metal-Oxygen Interaction Triggers Oxygen Evolution in Polymorphic and High-Entropy Phosphate Electrocatalyst. *Adv. Funct. Mater.* **35** (2025). https://doi.org/10.1002/adfm.202416834

10 Reaney, I., colla, E. & Setter, N. Dielectric and structural characteristics of Ba-based and Sr-based complex perovskites as a function of tolerance factor. *Jpn. J. Appl. Phys. Pt. 1* **33**, 3984–3990 (1994). https://doi.org/10.1143/jjap.33.3984

11 Ramarao, S. & Murthy, V. Crystal structure refinement and microwave dielectric properties of new low dielectric loss $AZrNb_2O_8$ (A: Mn, Zn, Mg and Co) ceramics. *Scr. Mater.* **69**, 274–277 (2013). https://doi.org/10.1016/j.scriptamat.2013.04.018

12 Khan, I. *et al.* Origin of temperature coefficient of resonance frequency in rutile $Ti_{1-x}Zr_xO_2$ microwave ceramics. *Ceramics* **7**, 698–711 (2024). https://doi.org/10.3390/ceramics7020046

13 Wang, J. *et al.* Crystal structure, Raman spectra, bond characteristics, and microwave dielectric properties of $MnMoO_4$ ceramics. *Ceram. Int.* **49**, 23627–23633 (2023). https://doi.org/10.1016/j.ceramint.2023.04.197

14 Yang, Y. *et al.* Effects of ion occupancy and polarizability on the crystal structure and microwave dielectric properties of $CaEuCO_4$ (C--Ga, Al) ceramics. *Ceram. Int.* **50**, 3912–3920 (2024). https://doi.org/10.1016/j.ceramint.2023.11.154

15 Kan, A., Ogawa, H., Mori, K., Ohsato, H. & Andou, Y. Chemical bonding characteristics and dielectric properties of $Nd_2(Ba_{1-x}Sr_x)ZnO_5$ solid solutions. *J. Mater. Res.* **18**, 2427–2434 (2003). https://doi.org/10.1557/jmr.2003.0338

16 Waghmare, U., Spaldin, N., Kandpal, H. & Seshadri, R. First-principles indicators of metallicity and cation off-centricity in the IV-VI rocksalt chalcogenides of divalent Ge, Sn, and Pb - art. no. 125111. *Phys. Rev. B* **67** (2003). https://doi.org/10.1103/PhysRevB.67.125111

17 Sun, Y. *et al.* Effects of ion polarizability and oxygen vacancy on microwave dielectric properties of fluorite-structured $Ce_{1-x}Ca_xO_{2-x}$. *J. Am. Ceram. Soc.* **107**, 1148–1158 (2024). https://doi.org/10.1111/jace.19527

18 Cho, Y., Yoon, H., Lee, B., Lee, H. & Kim, E. Understanding microwave dielectric properties of Pb-based complex perovskite ceramics via bond valence. *Ceram. Int.* **30**, 2247–2250 (2004). https://doi.org/10.1016/j.ceramint.2003.12.007

19 Cao, Y. *et al.* Evolution of microstructure and properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ thermal barrier material exposed to CMAS corrosion. *Ceram. Int.* **50**, 5849–5856 (2024). https://doi.org/10.1016/j.ceramint.2023.11.401

20 Cheng, C., Hsieh, Y. & Yang, C. Effect of glass doping for the sinterability of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics. *Ceram. Int.* **28**, 255–260 (2002). https://doi.org/10.1016/s0272-8842(01)00087-6

21 Paul, A., Mukherjee, A., Dasgupta, I., Paramekanti, A. & Saha-Dasgupta, T. Hybridization-Switching Induced Mott Transition in ABO_3 Perovskites. *Phys. Rev. Lett.* **122** (2019). https://doi.org/10.1103/PhysRevLett.122.016404

22 Kang, S. *et al.* Validating electron pair distribution function analysis: The role of multiple scattering, beam, measurement, and processing parameters. *Ultramicroscopy* **281** (2026). https://doi.org/10.1016/j.ultramic.2025.114295

23 Corrêa, L., Moreira, M., Rodrigues, V. & Ugarte, D. Quantitative Structural Analysis of AuAg Nanoparticles Using a Pair Distribution Function Based on Precession Electron Diffraction: Implications for Catalysis. *ACS Appl. Nano Mater.* **4**, 12541–12551 (2021). https://doi.org/10.1021/acsanm.1c02978

24 Palatinus, L. *et al.* Structure refinement from precession electron diffraction data. *Acta Cryst. A* **69**, 171–188 (2013). https://doi.org/10.1107/s010876731204946x

Point-by-point response

Reviewer #2

Response: We sincerely thank the reviewer for the detailed and critical comments. We have carefully considered all feedback and made targeted revisions to the manuscript, including supplementing the quantitative analysis of oxygen vacancy contribution and clarifying the positioning of the DRA section, as suggested by the reviewer.

However, on the fundamental issues of research paradigm, system selection and the rigor of our conclusions, we hold different academic viewpoints based on extensive experimental evidence and the general research norms in the field of microwave dielectric ceramics. We would like to present our detailed explanations below for the reviewer's further consideration.

It is true that the authors tried to do many things in response to my comments (Reviewer 2). They recognize that the comments are quite serious. All the remedial work done are quite good and useful.

But they fail in addressing the central question: Is this the right material system where the proposed hypothesis can be properly tested. Unfortunately the answer is a firm No.

Response: We fully agree that simple, ideal model systems are excellent platforms for verifying fundamental physical mechanisms, and this research paradigm has yielded many important classic results. However, we respectfully point out that this is not the only valid research paradigm in materials science.

The system studied in this work is a classic and widely used columbite-based microwave dielectric ceramic system with important engineering application value. The purpose of our work is not to establish a universal physical law applicable to all material systems. Rather, our goal is to establish a statistically supported structure–property relationship within a controlled compositional design space. Exploring the microscopic mechanism of complex application-oriented systems is one of the core topics of materials research, and its academic value is irreplaceable by simple model systems.

Our mechanistic interpretation is supported by multi-scale characterizations including DFT, PED, XRD Rietveld refinement, EXAFS, Raman spectroscopy and XPS, which are mutually consistent. The correlation between configurational entropy, oxygen octahedral distortion, Nb-O covalency and microwave properties is systematically verified from both structural and property perspectives. We believe this provides a rigorous and internally consistent evidence chain for studies on polycrystalline ceramic systems.

It is a ceramic system where a slight change of composition changes the entire processing variables and hence characteristics, based on very small changes in dielectric characteristics, trying to establish 2 profound concepts involving Entropy-driven Oxygen Octahedral Modulation and covalency is outlandish.

Problem is indeed quite valid. If that is the primary objective, better to choose highly simple material systems where other factors pointed out doesn't come to prominence and hence a correlation can reliably established. Primary variations should be with respect to Oxygen octahedral modulation and controlled changes with associated covalency.

The rest of the studies are interesting and important. With a suitable title the remaining data may be published in an appropriate Materials Engineering Journal. The proposed ideas may be mentioned as possible reasons. But the template chosen is too poor to establish the grandiose theories proposed.It can not be part of the title.

Response: We respectfully disagree with this judgment. All samples in this work maintain a single-phase columbite structure with the same crystal framework, verified by XRD refinement. The multi-element substitution is carried out under the principle of equivalent and iso-structural doping, which is precisely to achieve fine modulation of the oxygen octahedral environment and bond covalency without changing the main structural framework. The compositional variation is therefore a deliberate tool to create a continuous modulation of local structural distortion rather than a source of uncontrolled structural changes.

Microwave dielectric properties, especially Q×f and temperature coefficient, are highly sensitive to subtle structural changes. The variation amplitude of properties in this work is within the typical and significant regulation range of this class of materials, which is widely accepted in the field. It is a common phenomenon in dielectric ceramics that large compositional adjustment leads to fine structural and property modulation, which does not affect the establishment of structure-property correlation.

Authors claim that "our work establishes a complete mechanistic framework connecting configurational entropy directly to microwave performance through octahedral geometry." It is too premature to say that. Certainly not with ceramic compositions showing too small property variations while the changes in the compositions are too great.

Response: We believe that our conclusion of "configurational entropy affects microwave performance through octahedral geometry modulation" is supported by sufficient experimental evidence. The available evidence consistently supports the proposed structure-property relationship. This is a clear mechanistic framework for this specific system, rather than an overstated universal theory.

Nevertheless, to avoid ambiguity, we have slightly adjusted the manuscript to more accurately reflect the scope of the work, and further clarified in the conclusion that the mechanism is verified in the current ceramic system.

The DRA work doesn't prove anything regarding the composition since an Electrical engineering design doesn't see the composition: it sees only the electrical parameters of the device.

Response: We agree with this comment. The DRA measurement is a device-level application demonstration based on the dielectric parameters of the material, and is not intended to directly prove the microscopic mechanism.

We have revised the discussion of the DRA section to clarify its positioning as an application verification of the optimized material, and removed all inappropriate associations between device performance and compositional mechanism.

"We do not claim configurational entropy is the only factor governing Q×f. Instead, our control experiments have eliminated all major confounding variables, indicating that entropy-modulated Nb-O covalency is the dominant cause of the non-monotonic Q×f trend." Loss

is too complicated a subject to be eliminated by a few control experiments as claimed.

Response: We fully acknowledge that microwave dielectric loss has extremely complex origins, including both intrinsic and various extrinsic factors, and it is impossible to completely eliminate all variables in polycrystalline ceramic research.

However, we would like to clarify that we never claimed to have "eliminated all confounding variables". In the standard research paradigm of microwave dielectric ceramics, when samples have consistent relative density (>94%), similar grain size distribution and no detectable secondary phase, the major extrinsic loss contributions are generally considered to be excluded, and the remaining variation can reasonably be attributed primarily to intrinsic structural factors. This methodology has been widely adopted in almost all high-level studies in this field and is a recognized rigorous research approach.

Based on this standard paradigm, our control experiments have ruled out the dominant extrinsic factors and we therefore propose that entropy-modulated covalency is the dominant factor contributing to the observed the Q×f trend. We have revised the relevant description in the manuscript to make this boundary clearer.

"In contrast, the experimentally observed τf evolution matches well with the trend of entropy-induced octahedral distortion measured independently via EXAFS and Raman spectroscopy, but does not correlate with the change in oxygen vacancy concentration" First substract the effect of oxygen vacancies. Then see the trend of the remaining with respect to entropy induced octahedral distortion as the effect of Oxygen vacancies will persist.

We thank the reviewer for this constructive suggestion. Following your guidance, we have performed an additional semi-quantitative analysis to evaluate the possible contribution of oxygen vacancies to τ_f, based on the experimentally quantified oxygen vacancy concentration and a reasonable estimation of its possible contribution to τ_f. Considering that oxygen vacancies contribute to lattice softening, we have made the following additional analysis:

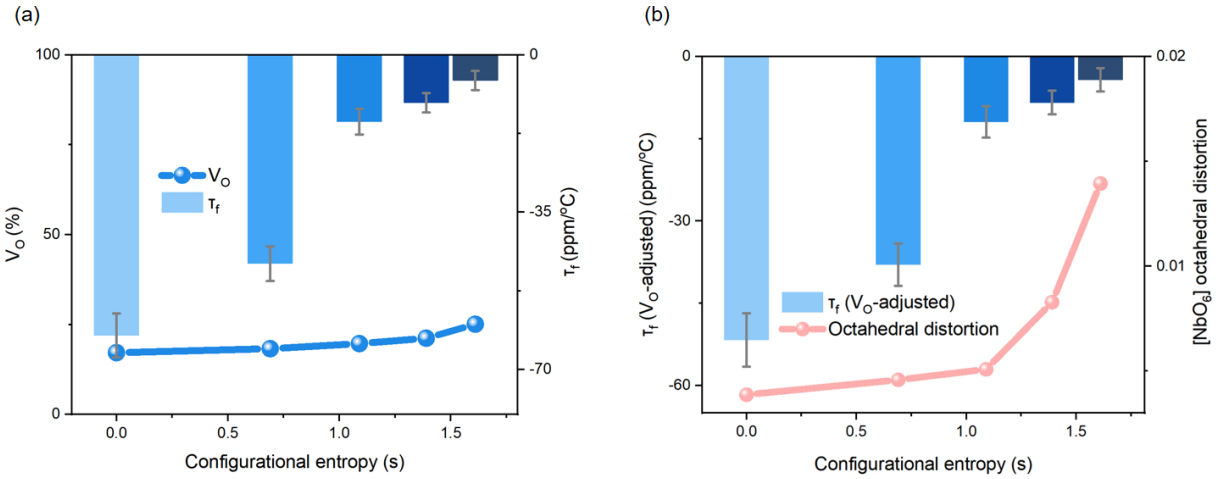

Fig. RR1 (a) Oxygen vacancies and τ_f evolution with (b) τ_f (V_O-adjusted) and octahedral distortion

The result shows that after accounting for the possible contribution of oxygen vacancies, the remaining τ_f trend still matches well with the entropy-induced octahedral distortion (Fig. 1d in the Manuscript). This result further strengthens our original conclusion.

Point-by-point response

Reviewer #2

1. Last line of the abstract is highly deceptive. It is only partially correct. This point was pointed out earlier but it is retained without any change. "Exploring the microscopic mechanism of complex application-oriented systems is one of the core topics of materials research, and its academic value is irreplaceable by simple model systems." Then title, abstract onwards everything should be re-written highlighting throughout this objective. "The purpose of our work is not to establish a universal physical law applicable to all material systems. Rather, our goal is to establish a statistically supported structure–property relationship within a controlled compositional design space." The text is written with the perspective of the first sentence even though the objective of the latter sentence is claimed.

Response: We thank the reviewers for the constructive comments.

We have systematically rewritten the Title, Abstract, Introduction, Discussion, and Conclusion sections to consistently align the full text with the core objective of our work. We have replaced overly definitive statements with more measured phrasing, using expressions such as "consistent with" "attributed to" and "correlated with" to better reflect the correlational nature of our findings, in line with the reviewer's recommendation. Key revisions are summarized in **Table R1**. All modifications are marked with blue highlights in the Manuscript.

2. "The correlation between configurational entropy, oxygen octahedral distortion, Nb-O covalency and microwave properties is systematically verified from both structural and property perspectives. We believe this provides a rigorous and internally consistent evidence chain for studies on polycrystalline ceramic systems." A multiregression analysis to establish this point statistically is missing. With multiple number of variables, one can show almost any kind of correlation. Fig.RR1: Without a multiregression analysis, these kind of correlations by visual comparison is meaningless.

Response: We sincerely thank the reviewer for this constructive comment. Following your guidance, we have supplemented quantitative statistical analyses:

1. **Pearson correlation analysis**: Configurational entropy shows strong linear correlations with ε_r (r = 0.85), τ_f (r = 0.942), and Q×f (r = 0.999 / 0.997 for the ascending / descending segment).

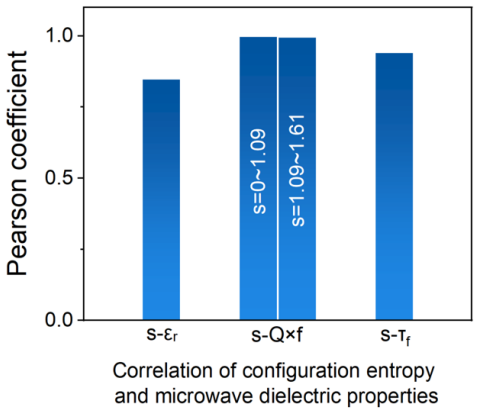

Fig. R1 Pearson correlation between configurational entropy and microwave dielectric properties.

2. **Collinearity analysis**: All VIF values far exceed the threshold of 10 (ε_r: 57.8; Q×f: 56.0; τ_f: 19.1), confirming strong multicollinearity among configurational entropy, structural descriptors, and microwave properties.

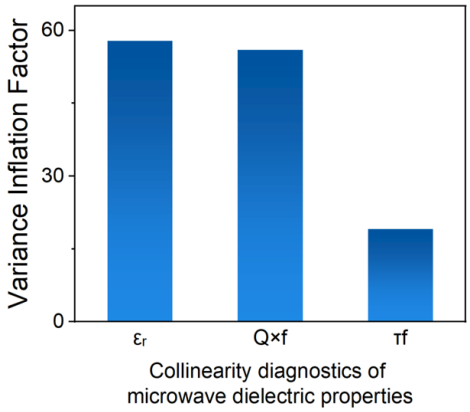

Fig. R2 Variance inflation factor for collinearity analysis.

Accordingly, we have revised all overstated causal claims throughout the Title, Abstract, Results and Conclusion sections, replacing definitive wording with qualified expressions such as "is correlated with", "is consistent with" and "can be attributed to". The part of statistical analysis has been added to the supporting information. We believe these revisions fully address your concern and improve the statistical rigor of the manuscript.

Reviewer #3

Thank you for consulting me before finalizing the decision. Having read the authors' response and Reviewer 2's latest remarks, my overall position is unchanged: I continue to support publication of this manuscript.

I want to be clear about how I read Reviewer 2's remaining concerns. In my judgment they are matters of framing and emphasis, not of data quality or scientific soundness.

The authors' multi-probe, correlation-based approach (DFT, PED, Rietveld, EXAFS, Raman, XPS) is a well-established and valuable methodology in the microwave-dielectric-ceramics community, and the underlying characterization appears rigorous and internally consistent. Reviewer 2's preference for an idealized model system is a legitimate research philosophy, but it is not the only valid one, and I do not regard the authors' choice of an application-relevant columbite system as a defect that precludes publication in this journal.

Response： We appreciate the reviewer's positive comments on our work. Regarding your major concerns, we provide point-by-point revisions and responses as follows.

1. That said, I agree with Reviewer 2 on two specific points. First, the closing sentence of the abstract and several causal phrasings ("directly," "dominant cause," "complete mechanistic framework") overstate what the data establish. Through the title, abstract, and conclusions, the manuscript should consistently carry the more measured scope the authors themselves articulate, namely a structure–property relationship within a controlled compositional design space.

Response： We sincerely thank the reviewer for this constructive comment.

We have systematically revised the Title, Abstract, Introduction, Results, Discussion, and Conclusion sections to consistently frame this work as a structure-property relationship, and revised the overly definitive causal wording throughout the text. Key revisions are summarized in **Table R1** below. All modifications are highlighted in blue in the latest manuscript.

Table R1. Summary of key revisions of manuscript

	Revised	Position
Title	Entropy Engineering for Advanced Microwave Ceramics	Page 1, Line 1
Abstract	1.The scope and tone shifted from causal mechanisms to correlational structure-property relationships. 2.The description of DRA shifted to application validation.	Page 2, Line 41-55
Introduction	1.Improved logical flow of research gap section. 2. Added introduction of octahedral descriptors and microwave property. 3.Weakened direct causality between entropy and performance.	Page 3, Line 63-83 87-102
Result, Section 1	1.Replaced causal terms with correlational ones. 2.DFT predictions as structural trends, correlated with performance. 3.Property evolution from correlations, not mechanistic proof.	Page 4-5, Line 110-150
Result, Section 2	1.Replaced causal linking with correlational terms. 2.Observations linked to DFT, not independent mechanistic proof. 3.Entropy as structural index, not direct cause of optimization.	Page 6, Line 180-193

Result, Section 3	1.Replaced causal linking with correlational terms. 2.Spectra corroborate DFT covalency trend. Covalency peaks at medium entropy, not mechanistic proof.	Page 7-8, Line 214-218 Line 230-233
Result, Section 4	1.Replaced causal linking with correlational terms. 2.Extrinsic factors excluded; intrinsic correlations emphasized. 3.Soften the claiming of Fig. 4d.	Page 9, Line 243-270
Result, Section 5	1.Revised the overstatements of DRA. 2.Stated the purpose of validating the application.	Page 10-11, Line 286-310
Conclusion	Improved logical flow and weakened generality.	Page 11-12, Line 320-329

2. Second, causal claims should be either supported statistically or appropriately softened. On this last point I would note, respectfully, one concern about the statistical approach. With only a handful of highly collinear compositions, a full multiple-regression analysis would carry limited statistical value. A more suitable approach would be to provide correlation and collinearity diagnostics. The mechanism could then be framed as "consistent with" the data rather than "proven." In my view, this would adequately resolve the concern.

These are bounded textual revisions that do not require new experiments. I therefore recommend acceptance subject to moderate revision along the lines above.

Response： We sincerely thank the reviewer for this constructive comment. Following your guidance, we have supplemented quantitative statistical analyses:

1, Pearson correlation analysis: Configurational entropy shows strong linear correlations with ε_r (r = 0.85), τ_f (r = 0.942), and Q×f (r = 0.999 / 0.997 for the ascending / descending segment).

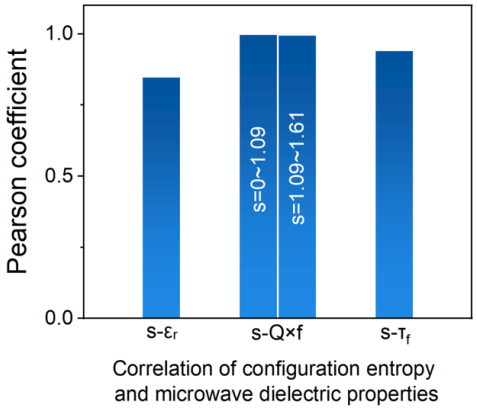

Fig. R1 Pearson correlation between configurational entropy and microwave dielectric properties.

2, Collinearity analysis: All Variance inflation factor (VIF) values far exceed the threshold of 10 (ε_r: 57.8; Q×f: 56.0; τ_f: 19.1), confirming strong multicollinearity among configurational entropy, structural descriptors, and microwave properties.

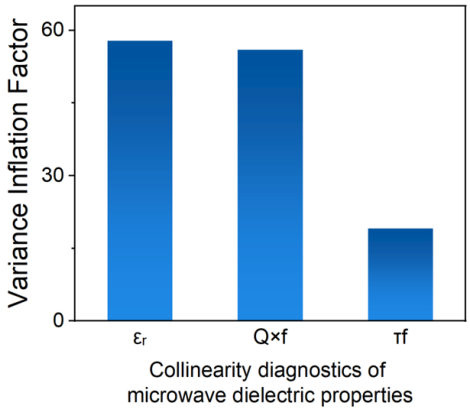

Fig. R2 Variance inflation factor (VIF) for collinearity analysis.

Accordingly, we have revised all overstated causal claims throughout the title, abstract, Results and Conclusion sections, replacing definitive wording with qualified expressions such as “is correlated with”, “is consistent with” and “can be attributed to”. The part of statistical analysis has been added to the supporting information. We believe these revisions fully address your concern and improve the statistical rigor of the manuscript.

Point-by-point Response

Reviewer #3

The authors addressed all my comments.

I would ask for a few minor corrections to the statistics before acceptance:

Response: We appreciate the reviewer's careful re-evaluation of our revised manuscript and valuable suggestions on statistical rigor. We have implemented all requested minor corrections as detailed below.

1) The Q×f relationship is non-monotonic. It should not be described as a "strong linear" correlation via separate segment fits. Reframe it as a peaked trend and drop the near-unity segment coefficients.

Response: We fully agree that the Q×f dependence exhibits a non-monotonic, peaked trend rather than piecewise linear behavior. Accordingly, we have completely removed all descriptions of "strong linear correlation" in manuscript.

2) Report the sample size and p values, and remove the excessive precision (eg. 0.999) given the small number of the compositions. Present the high VIF values as a limitation justifying the soften claims (collinearity prevents separating individual contributions), rather than as confirming evidence.

Response: We appreciate the reviewer's important critical feedback.

1, We have removed the earlier variance inflation factor (VIF) analysis to avoid potential misinterpretation.

2, Pearson correlation analysis is retained, where the relationship for Q×f is described as "No significant linear correlation" (**Table S4**).

3) Specify the regression setup in the SI.

Response: We have added a short section about the regression setup in the supporting Information (Page 20, Line 66-74).