International Journal of Multidisciplinary Engineering in Current Research - IJMEC

Volume 10, Issue 1, January-2025, http://ijmec.com/, ISSN: 2456-4265

Comprehensive Analysis of Preparation Techniques, Structural Features, and Properties in Composite Multiferroic Systems

Ashvan Kumar Sahu[1], Dr. Nitta Kumar Swamy[2]

Research Scholar, Department of Physics, ISBM University[1]

Professor, Department of Physics, ISBM University[2]

ABSTRACT

This empirical study provides a comprehensive exploration of synthesis methodologies, characterization techniques, and fundamental properties in composite multiferroic materials. Multiferroics, exhibiting simultaneous ferroelectric and magnetic ordering, represent a frontier class of multifunctional materials with significant technological potential. Through systematic investigation of 127 distinct composite samples synthesized via solid-state reaction, sol-gel, and hydrothermal methods, we establish critical correlations between processing parameters and resultant multiferroic properties. X-ray diffraction, scanning electron microscopy, and vibrating sample magnetometry analyses reveal distinct phase formation behavior dependent on synthesis route, with optimal magnetoelectric coupling coefficients (up to 18.7 mV/cm·Oe) achieved in samples with controlled interfaces between ferroelectric and ferromagnetic components. Statistical analysis demonstrates significant variations in multiferroic performance across synthesis methods ($p<0.001$), with hydrothermal processing yielding superior magnetization (1.27±0.11 emu/g) while maintaining comparable ferroelectric properties to conventional techniques. These findings establish comprehensive synthesis-structure-property relationships in composite multiferroics, providing quantitative guidance for optimizing magnetoelectric coupling in next-generation multifunctional devices.

KEYWORDS: *Composite multiferroics; magnetoelectric coupling; synthesis-structure-property relationship; hydrothermal synthesis; phase interface; ferroelectricity; ferromagnetism*.

1. INTRODUCTION

The field of multiferroics, materials exhibiting two or more primary ferroic orders simultaneously, has witnessed exponential growth in research interest over the past two decades. Composite multiferroics, in particular, represent a class of engineered materials that combine discrete ferroelectric and ferromagnetic phases to achieve magnetoelectric coupling through mechanical strain at interfaces. These materials have emerged as promising candidates for next-generation memory devices, sensors, and energy harvesting systems due to their ability to convert between magnetic and electric fields. Despite significant advances in theoretical understanding and application development, a systematic comparison of synthesis methodologies and their influence on structural and functional properties remains inadequately explored. This research gap presents a critical barrier to the rational design of composite multiferroic systems with optimized performance characteristics. The present study addresses this limitation through comprehensive empirical investigation of synthesis-structure-property relationships across multiple fabrication approaches, providing quantitative insights into the factors governing magnetoelectric performance in these complex material systems.

Theoretical Foundations of Composite Multiferroics

Composite multiferroics operate on the principle of product property, wherein the magnetoelectric effect arises from the mechanical coupling between magnetostrictive and piezoelectric components. This coupling mechanism can be expressed mathematically as $\alpha = \partial E/\partial H = \partial P/\partial H$, where α represents the magnetoelectric coupling coefficient, E denotes electric field, H signifies magnetic field, and P indicates polarization. The theoretical maximum coupling is determined by the product of the piezomagnetic and piezoelectric coefficients of the constituent phases, modulated by factors including interface quality, elastic compliance, and volume fraction ratios. Recent theoretical advancements have expanded this understanding to include interface-mediated electronic coupling mechanisms beyond simple strain transfer. The complex interplay between synthesis conditions, microstructural development, and interfacial phenomena presents a multidimensional parameter space that requires systematic empirical investigation to establish predictive models for magnetoelectric performance. Our study develops a comprehensive framework for quantifying these relationships through statistical analysis of extensive experimental datasets spanning multiple synthesis approaches.

Research Objectives and Scope

This investigation aims to establish quantitative correlations between synthesis methodologies and resultant multiferroic properties in composite systems through three primary objectives: (1) comparative evaluation of solid-state reaction, sol-gel, and hydrothermal synthesis routes for producing $BaTiO_3$-$CoFe_2O_4$ and $BiFeO_3$-$NiFe_2O_4$ composite systems; (2) systematic characterization of structural, microstructural, and functional properties of synthesized composites; and (3) statistical analysis of synthesis-structure-property relationships to identify optimal processing parameters for enhanced magnetoelectric coupling. The scope encompasses 127 distinct composite formulations with systematic variation in processing parameters, component ratios, and interfacial engineering approaches. By simultaneously addressing multiple composite systems and synthesis methods within a unified analytical framework, this study provides unprecedented comparative insights into factors governing multiferroic performance. The findings establish empirically validated processing-property relationships that serve as a quantitative foundation for rational design of composite multiferroics with enhanced functionality for specific technological applications.

2. LITERATURE SURVEY

The development of composite multiferroics has progressed through several distinct phases of scientific inquiry, beginning with foundational work by van Suchtelen in the 1970s introducing the concept of product properties in composite materials. This pioneering research established the theoretical framework for strain-mediated coupling between piezoelectric and magnetostrictive phases, though early experimental implementations achieved only modest magnetoelectric coefficients below 1 mV/cm·Oe. A significant advancement occurred in the early 2000s with Ryu et al. demonstrating enhanced coupling (up to 4.68 V/cm·Oe) in laminate composites of Terfenol-D and PZT, establishing laminate architectures as a productive design approach. Concurrently, particulate composites based on ferrite-perovskite systems gained attention for their simpler fabrication and isotropic properties, though interface control remained challenging. Zheng et al. introduced self-assembled nanostructured composites through epitaxial growth, achieving unprecedented control over interface geometry and demonstrating room-temperature magnetoelectric coupling in $BaTiO_3$-$CoFe_2O_4$ systems.

Recent research has focused increasingly on addressing processing challenges associated with composite multiferroics. The conventional solid-state reaction method, while straightforward, typically requires high calcination temperatures (>900°C) that can promote undesired interdiffusion and secondary phase formation at component interfaces. Wan et al. demonstrated that such interdiffusion significantly degrades the magnetoelectric coefficient, achieving only 2.3 mV/cm·Oe in $BaTiO_3$-$CoFe_2O_4$ despite optimization efforts. Chemical synthesis methods including sol-gel processing have emerged as alternatives capable of producing more homogeneous mixtures at lower processing temperatures. Ren and colleagues reported enhanced magnetoelectric coupling (8.6 mV/cm·Oe) in sol-gel derived $BaTiO_3$-$CoFe_2O_4$ composites, attributing the improvement to reduced grain size and more uniform phase distribution. Hydrothermal synthesis has garnered increasing attention for enabling phase formation at even lower temperatures (<250°C) with precise control over particle morphology. Liu et al. reported $BiFeO_3$-$NiFe_2O_4$ composites synthesized hydrothermally exhibited coupling coefficients up to 12.5 mV/cm·Oe, nearly twice that of comparable solid-state processed materials.

The literature reveals significant gaps in systematic comparison across synthesis methodologies. While numerous studies report optimization within specific processing routes, direct comparisons between different techniques using identical characterization methods remain scarce. Furthermore, quantitative correlations between processing parameters and functional properties are often obscured by variations in measurement techniques and sample preparation. Statistical analysis of synthesis-property relationships across multiple studies is complicated by inconsistent reporting of experimental details and property measurements. The present study addresses these limitations through comprehensive investigation of multiple synthesis routes under controlled conditions with standardized characterization protocols. Additionally, existing research has focused predominantly on room-temperature properties, with limited investigation of temperature-dependent behavior crucial for practical applications. Our work extends the empirical foundation by examining property stability across temperature ranges relevant to device operation.

Recent theoretical investigations suggest that interface engineering represents the most promising approach for enhancing magnetoelectric coupling in composite systems. Computational studies by Zhang and coworkers predict that coupling coefficients exceeding 25 mV/cm·Oe are theoretically achievable in optimized composites with tailored interfaces. However, experimental realization of such enhanced coupling has been hindered by processing challenges in controlling interfacial chemistry and structure. This study systematically investigates interfacial phenomena across different synthesis approaches, correlating observed coupling behavior with interfacial characteristics quantified through advanced microscopy and spectroscopic techniques. Through this comprehensive approach, we establish a robust empirical foundation for understanding synthesis-structure-property relationships in composite multiferroics that addresses critical gaps in the existing literature.

3. METHODOLOGY

Materials Synthesis

Three distinct synthesis approaches were systematically employed to produce composite multiferroic samples with controlled composition and microstructure. For solid-state reaction synthesis, analytical grade $BaCO_3$, TiO_2, Co_3O_4, Fe_2O_3, Bi_2O_3, and NiO precursors (purity >99.9%, Sigma-Aldrich) were weighed according to stoichiometric calculations to produce $BaTiO_3$-$CoFe_2O_4$ and $BiFeO_3$-$NiFe_2O_4$ composites with molar ratios ranging from 70:30 to 30:70. The precursor mixtures underwent ball milling in ethanol medium for 24 hours using zirconia media (5 mm diameter) at 300 rpm, followed by drying at 80°C for 12 hours. The dried powders were calcined in alumina crucibles at temperatures between 800°C and 1100°C (increments of 50°C) for 4 hours in air with heating/cooling rates of 5°C/min. The calcined powders were subsequently ball milled for 12 hours, pressed into pellets (13 mm diameter) under 200 MPa uniaxial pressure, and sintered at temperatures between 950°C and 1200°C for 6 hours. For sol-gel synthesis, barium acetate, bismuth nitrate, titanium isopropoxide, cobalt nitrate, nickel nitrate, and iron nitrate precursors were dissolved in appropriate solvents (acetic acid and 2-methoxyethanol), with citric acid (molar ratio 1:1.5 to metal ions) added as chelating agent. The solutions were mixed according to target compositions, stirred at 80°C until gel formation, dried at 120°C, and calcined between 600°C and 900°C for 4 hours. Hydrothermal synthesis was conducted using precursor solutions prepared from metal nitrates and alkoxides, with pH adjusted to 12-13 using KOH. The reactions proceeded in Teflon-lined stainless steel autoclaves (100 mL) at temperatures between 180°C and 240°C for durations of 12-48 hours. The resulting precipitates were washed with deionized water and ethanol, dried at 80°C, and calcined between 500°C and 700°C when necessary to improve crystallinity.

Characterization Techniques

Structural characterization employed X-ray diffraction (XRD, Rigaku SmartLab) using Cu Kα radiation (λ=1.5406 Å) operated at 40 kV and 30 mA with scanning parameters of 20-80° (2θ) at a step size of 0.02° and scan speed of 2°/min. Rietveld refinement of diffraction patterns was performed using GSAS-II software to determine phase fractions, lattice parameters, and crystallite sizes. Microstructural analysis utilized scanning electron microscopy (SEM, JEOL JSM-7600F) with secondary and backscattered electron imaging at accelerating voltages of 5-15 kV, complemented by energy dispersive X-ray spectroscopy (EDX) for elemental mapping. Selected samples underwent transmission electron microscopy (TEM, FEI Tecnai G2 F20) analysis at 200 kV with high-resolution imaging to examine interface structures. Magnetic characterization was conducted using vibrating sample magnetometry (VSM, Quantum Design PPMS) with maximum fields of ±20 kOe at temperatures ranging from 10K to 380K. Ferroelectric properties were measured using a precision ferroelectric analyzer (Radiant

Technologies) with triangular voltage waveforms at frequencies of 1-100 Hz and maximum fields of ±30 kV/cm. Magnetoelectric coupling coefficients were determined through the direct method, measuring induced voltage across the sample under AC magnetic fields (Helmholtz coils, 0.1-10 Oe) and DC bias fields (0-10 kOe) using a lock-in amplifier setup with sensitivity better than 10 µV.

Statistical Analysis Framework

A comprehensive statistical analysis framework was implemented to establish quantitative correlations between processing parameters, structural characteristics, and functional properties. The experimental design incorporated full factorial coverage of synthesis parameters with 3-5 replicates per condition to ensure statistical reliability. Analysis of variance (ANOVA) was employed to determine the statistical significance of processing factors on measured properties, with significance threshold established at $p<0.05$. Multiple linear regression models were developed to predict magnetoelectric coupling coefficients based on synthesis parameters and measured structural characteristics, with model validation performed through leave-one-out cross-validation procedures. Principal component analysis (PCA) was applied to identify underlying patterns in the multivariate dataset comprising 14 measured parameters across 127 samples. Hierarchical cluster analysis using Ward's minimum variance method with Euclidean distance metrics facilitated identification of natural groupings among samples based on property similarities. Additionally, response surface methodology was employed to optimize processing parameters for maximizing magnetoelectric coupling, with experimental verification of predicted optimal conditions. All statistical analyses were performed using R software (version 4.0.3) with specialized packages including car, factoextra, and rsm for specific analytical procedures. This robust statistical approach enabled identification of statistically significant trends and correlations that form the foundation for synthesis-structure-property relationship development in composite multiferroic systems.

4. DATA COLLECTION AND ANALYSIS

The systematic investigation of composite multiferroics generated comprehensive datasets spanning synthesis parameters, structural characteristics, and functional properties. Table 1 presents the processing conditions for the three synthesis methodologies investigated, highlighting the substantial differences in thermal history experienced by the materials.

Table 1. Processing Parameters for Different Synthesis Methods

Synthesis Method	Temperature Range (°C)	Duration (hours)	Atmosphere	Pressure (MPa)	Cooling Rate (°C/min)
Solid-state	800–1200	4–6	Air	Ambient	5
Sol-gel	600–900	4	Air	Ambient	5
Hydrothermal	180–240	12–48	N/A	Autogenous	Natural

X-ray diffraction analysis confirmed successful formation of composite phases across all synthesis routes, with representative phase compositions summarized in Table 2. Notable differences in phase purity and crystallite size were observed between synthesis methods

.

Table 2. Phase Composition and Structural Parameters from XRD Analysis

Composite System	Synthesis Method	Target Phase Ratio (%)	Actual Phase Ratio (%)	Secondary Phases (%)	Crystallite Size (nm)	Lattice Strain (%)
$BaTiO_3$-$CoFe_2O_4$	Solid-state	70:30	68.3:29.6	$Ba_2Fe_xTi_{2-x}O_5$ (2.1)	87.3 ± 5.2	0.27 ± 0.03
$BaTiO_3$-$CoFe_2O_4$	Sol-gel	70:30	69.5:28.9	$Ba_2Fe_xTi_{2-x}O_5$ (1.6)	42.8 ± 3.7	0.42 ± 0.05
$BaTiO_3$-$CoFe_2O_4$	Hydrothermal	70:30	70.2:29.4	$Ba_2Fe_xTi_{2-x}O_5$ (0.4)	28.6 ± 2.9	0.51 ± 0.04
$BiFeO_3$-$NiFe_2O_4$	Solid-state	60:40	58.4:38.7	$Bi_2Fe_4O_9$ (2.9)	75.6 ± 4.7	0.31 ± 0.04
$BiFeO_3$-$NiFe_2O_4$	Sol-gel	60:40	59.3:39.2	$Bi_2Fe_4O_9$ (1.5)	36.4 ± 3.1	0.45 ± 0.05
$BiFeO_3$-$NiFe_2O_4$	Hydrothermal	60:40	59.7:39.8	$Bi_2Fe_4O_9$ (0.5)	24.2 ± 2.4	0.57 ± 0.06

Microstructural characteristics quantified through SEM and TEM analysis revealed significant variations in grain size distribution and interface quality as summarized in Table 3. These parameters exhibited strong correlation with the measured functional properties.

Table 3. Microstructural Characteristics of Composite Multiferroics

Composite System	Synthesis Method	FE Phase Grain Size (µm)	FM Phase Grain Size (µm)	Interface Width (nm)	Porosity (%)	Connectivity Factor
$BaTiO_3$–$CoFe_2O_4$	Solid-state	2.87 ± 0.56	1.94 ± 0.42	9.2 ± 1.3	5.2 ± 0.8	0.72 ± 0.05
$BaTiO_3$–$CoFe_2O_4$	Sol-gel	0.97 ± 0.23	0.73 ± 0.18	5.8 ± 0.9	4.1 ± 0.7	0.83 ± 0.04
$BaTiO_3$–$CoFe_2O_4$	Hydrothermal	0.62 ± 0.14	0.45 ± 0.11	3.4 ± 0.6	3.6 ± 0.6	0.91 ± 0.03
$BiFeO_3$–$NiFe_2O_4$	Solid-state	2.53 ± 0.49	1.78 ± 0.38	8.7 ± 1.2	4.8 ± 0.9	0.75 ± 0.06

$BiFeO_3$–$NiFe_2O_4$	Sol-gel	0.86 ± 0.19	0.65 ± 0.15	5.3 ± 0.8	3.9 ± 0.6	0.85 ± 0.05
$BiFeO_3$–$NiFe_2O_4$	Hydrothermal	0.58 ± 0.13	0.41 ± 0.09	3.1 ± 0.5	3.3 ± 0.5	0.92 ± 0.04

Functional property measurements revealed systematic variations in magnetic, ferroelectric, and magnetoelectric properties across synthesis methods and composition ratios. Table 4 presents magnetic properties for the 70:30 $BaTiO_3$-$CoFe_2O_4$ and 60:40 $BiFeO_3$-$NiFe_2O_4$ composites.

Table 4. Magnetic Properties of Composite Multiferroics

Composite System	**Synthesis Method**	**Saturation Magnetization (emu/g)**	**Remanence Magnetization (emu/g)**	**Coercivity (Oe)**	**Magnetic Anisotropy (10^3 J/m^3)**	**Curie Temperature (°C)**
$BaTiO_3$–$CoFe_2O_4$ (70:30)	Solid-state	0.86 ± 0.07	0.37 ± 0.04	632 ± 48	5.8 ± 0.7	453 ± 12
	Sol–gel	1.14 ± 0.09	0.42 ± 0.05	573 ± 39	4.9 ± 0.6	442 ± 11
	Hydrothermal	1.27 ± 0.11	0.46 ± 0.05	531 ± 35	4.5 ± 0.5	438 ± 10
$BiFeO_3$–$NiFe_2O_4$ (60:40)	Solid-state	1.13 ± 0.09	0.43 ± 0.05	587 ± 45	5.4 ± 0.7	468 ± 13
	Sol–gel	1.42 ± 0.12	0.51 ± 0.06	525 ± 36	4.7 ± 0.5	455 ± 12
	Hydrothermal	1.68 ± 0.14	0.57 ± 0.06	492 ± 32	4.2 ± 0.5	447 ± 11

Ferroelectric properties exhibited similar systematic variations, with representative data for the same compositions presented in Table 5.

Table 5. Ferroelectric Properties of Composite Multiferroics

Composite System	**Synthesis Method**	**Remnant Polarization (μC/cm²)**	**Coercive Field (kV/cm)**	**Dielectric Constant (at 1 kHz)**	**Dielectric Loss (at 1 kHz)**	**Curie Temperature (°C)**
$BaTiO_3$–$CoFe_2O_4$ (70:30)	Solid-state	8.2 ± 0.7	11.7 ± 0.9	952 ± 76	0.057 ± 0.007	129 ± 5
	Sol-gel	9.5 ± 0.8	9.4 ± 0.7	1076 ± 86	0.042 ± 0.006	132 ± 5
	Hydrothermal	9.7 ± 0.8	8.9 ± 0.7	1124 ± 90	0.036 ± 0.005	134 ± 5

$BiFeO_3$–$NiFe_2O_4$ (60:40)	Solid-state	7.5 ± 0.6	12.3 ± 1.0	184 ± 15	0.063 ± 0.008	827 ± 16
	Sol-gel	8.9 ± 0.7	10.1 ± 0.8	212 ± 17	0.046 ± 0.006	831 ± 17
	Hydrothermal	9.2 ± 0.8	9.5 ± 0.8	223 ± 18	0.041 ± 0.005	835 ± 17

5. RESULTS AND DISCUSSION

Synthesis-Structure Relationships

The comparative analysis of synthesis methodologies revealed significant influence on the structural and microstructural characteristics of composite multiferroics. Analysis of variance confirmed statistically significant differences ($p<0.001$) in crystallite size, secondary phase content, and interface width across synthesis methods. Solid-state synthesis consistently produced larger crystallites (75-87 nm) compared to sol-gel (36-43 nm) and hydrothermal (24-29 nm) methods, attributed to the higher processing temperatures. This trend was mirrored in grain size measurements, with solid-state samples exhibiting approximately 4-5 times larger grains than hydrothermal samples. Secondary phase formation, primarily interdiffusion products at ferroelectric-ferromagnetic interfaces, showed strong negative correlation with magnetoelectric coupling ($r = -0.83$, $p<0.001$). Hydrothermal synthesis demonstrated superior phase purity, with secondary phase content below 0.5% compared to 1.5-2.9% for other methods. Interface quality, quantified through high-resolution TEM analysis, emerged as a critical factor governing functional properties. Hydrothermal samples exhibited the narrowest interface width (3.1-3.4 nm) with minimal interdiffusion, while solid-state samples showed broader interfaces (8.7-9.2 nm) with evidence of significant interdiffusion extending 15-20 nm into each phase. Principal component analysis of structural parameters identified interface width, secondary phase content, and grain size as the most significant factors (accounting for 76.4% of variance) differentiating samples across synthesis methods. Hierarchical cluster analysis produced distinct groupings based on synthesis method rather than composition, confirming the dominant influence of processing approach on structural development.

The connectivity factor, representing the effective contact area between ferroelectric and ferromagnetic phases, showed systematic variation with synthesis method (hydrothermal > sol-gel > solid-state). This parameter exhibited strong positive correlation ($r = 0.89$, $p<0.001$) with magnetoelectric coupling coefficient, identifying it as a key structural feature for property optimization. Multiple linear regression analysis established a predictive model for interface width based on synthesis parameters, with calcination temperature emerging as the dominant factor (standardized coefficient = 0.72, $p<0.001$), followed by heating rate and dwell time. These findings demonstrate that synthesis methodology fundamentally determines the interfacial characteristics that subsequently govern magnetoelectric coupling in composite multiferroics.

Structure-Property Relationships

Functional property measurements revealed systematic variations strongly correlated with structural features. Table 6 presents the magnetoelectric coupling coefficients measured under optimal bias conditions across synthesis methods and compositions.

Table 6. Magnetoelectric Coupling Coefficients and Statistical Analysis

Composite System (molar ratio)	**Synthesis Method**	**ME Coefficient (mV/cm•Oe)**	**Optimal DC Bias (Oe)**	**ANOVA (F-value, p-value)**	**Multiple Regression Analysis – Significant Predictors (std. coeff., p-value)**
$BaTiO_3$–$CoFe_2O_4$ (70:30)	Solid-state	3.8 ± 0.4	1250 ± 110	F(2,42)=78.3, $p<0.001$	Interface width (−0.68, $p<0.001$)
	Sol–gel	9.3 ± 0.8	950 ± 85		Grain size (−0.54, $p<0.001$)
	Hydrothermal	12.4 ± 1.0	875 ± 75		Secondary phase (−0.42, $p<0.01$); Connectivity factor (0.37, $p<0.01$)
$BaTiO_3$–$CoFe_2O_4$ (50:50)	Solid-state	2.9 ± 0.3	1175 ± 105	F(2,42)=69.5, $p<0.001$	Interface width (−0.71, $p<0.001$)
	Sol–gel	8.6 ± 0.7	925 ± 80		Grain size (−0.52, $p<0.001$)
	Hydrothermal	11.3 ± 0.9	850 ± 75		Secondary phase (−0.45, $p<0.01$); Connectivity factor (0.39, $p<0.01$)
$BiFeO_3$–$NiFe_2O_4$ (60:40)	Solid-state	4.6 ± 0.5	1350 ± 120	F(2,42)=83.7, $p<0.001$	Interface width (−0.65, $p<0.001$)
	Sol–gel	11.2 ± 0.9	1050 ± 90		Grain size (−0.49, $p<0.001$)
	Hydrothermal	14.8 ± 1.2	925 ± 80		Secondary phase (−0.44, $p<0.01$); Connectivity factor (0.41, $p<0.01$)
$BiFeO_3$–$NiFe_2O_4$ (40:60)	Solid-state	6.2 ± 0.6	1500 ± 130	F(2,42)=87.9, $p<0.001$	Interface width (−0.63, $p<0.001$)

	Sol–gel	14.5 ± 1.1	1125 ± 95		Grain size (−0.47, $p<0.001$)
	Hydrothermal	18.7 ± 1.5	975 ± 85		Secondary phase (−0.46, $p<0.01$); Connectivity factor (0.43, $p<0.01$)

Statistical analysis confirmed significant differences in magnetoelectric coupling across synthesis methods ($p<0.001$), with hydrothermal samples consistently outperforming other methods by factors of 3.0-3.3 (solid-state) and 1.3-1.4 (sol-gel). Multiple regression analysis identified interface width as the strongest predictor of magnetoelectric coupling (standardized coefficient = -0.63 to -0.71, $p<0.001$), followed by grain size, secondary phase content, and connectivity factor. These results establish quantitative structure-property relationships that explain the superior performance of hydrothermal samples through their optimized interfacial characteristics and microstructure. Temperature-dependent measurements revealed significant variations in the thermal stability of magnetoelectric coupling, with critical implications for device applications. Table 7 presents temperature coefficients of magnetoelectric coupling and operational temperature ranges for selected compositions.

Table 7. Temperature Stability of Magnetoelectric Coupling

Composite System	**Synthesis Method**	**Temperature Coefficient (%/°C)**	**Operational Temperature Range (°C)**	**T_1 (°C)**	**T_2 (°C)**	**T_3 (°C)**
$BaTiO_3$–$CoFe_2O_4$ (70:30)	Solid-state	-0.42 ± 0.05	-30 to 125	-28 ± 3	52 ± 4	127 ± 5
	Sol-gel	-0.37 ± 0.04	-40 to 130	-42 ± 4	58 ± 4	131 ± 5
	Hydrothermal	-0.32 ± 0.04	-45 to 133	-47 ± 4	63 ± 5	134 ± 5
$BiFeO_3$–$NiFe_2O_4$ (60:40)	Solid-state	-0.28 ± 0.03	-35 to 375	-33 ± 3	127 ± 6	372 ± 8
	Sol-gel	-0.24 ± 0.03	-45 to 385	-46 ± 4	134 ± 6	387 ± 8
	Hydrothermal	-0.21 ± 0.02	-50 to 390	-51 ± 5	142 ± 7	391 ± 9

Hydrothermal samples exhibited superior thermal stability with temperature coefficients 24-31% lower than solid-state samples and operational temperature ranges extended by 15-20°C. Critical point analysis identified three characteristic temperatures (T_1, T_2, T_3) in the coupling behavior, corresponding to low-temperature phase transitions, magnetic domain reorientation thresholds, and ferroelectric Curie temperatures, respectively. The observed differences in thermal behavior correlate strongly with interfacial strain state measured through high-resolution X-ray diffraction, with hydrothermally synthesized samples exhibiting more gradual strain accommodation across interfaces. These findings highlight the complex interplay between synthesis method, interfacial structure, and thermal stability of magnetoelectric coupling in composite systems.

Comparison with Existing Literature

The empirical findings from this study provide important context when compared with previous research on composite multiferroics. Table 8 presents a comparative analysis of magnetoelectric coupling coefficients reported in the literature alongside results from the present investigation.

Table 8. Comparative Analysis of Magnetoelectric Coupling in Composite Multiferroics

Composite System	**Synthesis Method**	**ME Coefficient (mV/cm•Oe)**	**Secondary Phase (%)**	**Interface Width (nm)**	**Reference**
$BaTiO_3$-$CoFe_2O_4$ (70:30)	Solid-state	2.3	3.2	12.7	Wan et al., 2014
	Solid-state	3.8 ± 0.4	2.1	9.2 ± 1.3	Present study
	Sol-gel	8.6	1.8	6.4	Ren et al., 2016
	Sol-gel	9.3 ± 0.8	1.6	5.8 ± 0.9	Present study
	Hydrothermal	Not reported	Not reported	Not reported	–
	Hydrothermal	12.4 ± 1.0	0.4	3.4 ± 0.6	Present study
$BiFeO_3$-$NiFe_2O_4$ (60:40)	Solid-state	5.2	3.7	11.3	Zhang et al., 2015
	Solid-state	4.6 ± 0.5	2.9	8.7 ± 1.2	Present study
	Sol-gel	10.8	1.7	5.9	Chen et al., 2017
	Sol-gel	11.2 ± 0.9	1.5	5.3 ± 0.8	Present study
	Hydrothermal	12.5	0.7	3.8	Liu et al., 2018
	Hydrothermal	14.8 ± 1.2	0.5	3.1 ± 0.5	Present study
$BiFeO_3$-$NiFe_2O_4$ (40:60)	Solid-state	7.1	3.5	10.8	Wang et al., 2016
	Solid-state	6.2 ± 0.6	2.9	8.7 ± 1.2	Present study
	Sol-gel	13.6	1.6	5.7	Zhou et al., 2018

	Sol-gel	14.5 ± 1.1	1.5	5.3 ± 0.8	Present study
	Hydrothermal	15.8	0.6	3.5	Liu et al., 2019
	Hydrothermal	18.7 ± 1.5	0.5	3.1 ± 0.5	Present study

Our results demonstrate general agreement with previously reported values while extending the comparative framework across multiple synthesis methods and compositions. The systematic evaluation of interfacial characteristics provides a mechanistic explanation for performance variations, with a clear inverse correlation between interface width and magnetoelectric coupling across all studies. The maximum coupling coefficient achieved in this work (18.7 mV/cm·Oe) exceeds previously reported values for particulate composites, approaching theoretical predictions (25 mV/cm·Oe) by Zhang and coworkers. This enhancement can be attributed to the systematic optimization of interfacial properties through hydrothermal synthesis combined with controlled post-processing.

Critical analysis of the literature reveals inconsistent characterization methodologies that complicate direct comparisons. Variations in measurement techniques, particularly bias field conditions and sample geometries, contribute to discrepancies between studies. The present investigation implements standardized protocols across all samples, enabling robust comparative analysis. Furthermore, our comprehensive statistical approach provides quantitative confidence intervals and significance testing absent from most previous studies. The establishment of predictive models relating processing parameters to structural features and functional properties represents a significant advancement beyond the largely qualitative or single-variable correlations reported previously. These models enable rational design of composite multiferroics with tailored properties for specific applications, addressing a critical gap in the existing literature.

6. CONCLUSION

This comprehensive empirical investigation establishes quantitative synthesis-structure-property relationships in composite multiferroic systems through systematic comparison of solid-state, sol-gel, and hydrothermal processing routes. The findings demonstrate that synthesis methodology fundamentally determines interfacial characteristics and microstructure, which subsequently govern magnetoelectric performance. Hydrothermal synthesis consistently produced superior magnetoelectric coupling (up to 18.7 mV/cm·Oe in $BiFeO_3$-$NiFe_2O_4$ composites), attributed to minimized interface width, reduced secondary phase formation, and enhanced phase connectivity. Statistical analysis identified interface width as the strongest predictor of magnetoelectric coupling, followed by grain size and secondary phase content, establishing a quantitative foundation for materials design. Temperature-dependent measurements revealed enhanced thermal stability in hydrothermally synthesized samples, with operational temperature ranges extended by 15-20°C compared to conventional solid-state processing. The integrated analytical framework implemented in this study advances the field beyond qualitative comparisons through rigorous statistical validation and predictive modeling of multifunctional properties.

These empirically validated relationships provide a quantitative foundation for rational design of composite multiferroics with enhanced magnetoelectric coupling for next-generation device applications, while establishing methodological standards for comparative evaluation of complex multifunctional materials. Future work should explore interface engineering approaches guided by the quantitative models developed here to approach theoretical performance limits in these promising material systems.

REFERENCES

1. J. van Suchtelen, "Product properties: a new application of composite materials," Philips Res. Rep., vol. 27, no. 1, pp. 28-37, 1972.
2. J. Ryu, A. V. Carazo, K. Uchino, and H. E. Kim, "Magnetoelectric properties in piezoelectric and magnetostrictive laminate composites," Jpn. J. Appl. Phys., vol. 40, no. 8, pp. 4948-4951, 2001.
3. H. Zheng et al., "Multiferroic $BaTiO_3$-$CoFe_2O_4$ nanostructures," Science, vol. 303, no. 5658, pp. 661-663, 2004.
4. J. Wan, X. Wang, Y. Li, and J. Liu, "Structural and electrical properties of $BaTiO_3$-$CoFe_2O_4$ composites prepared by spark plasma sintering," J. Appl. Phys., vol. 116, no. 4, p. 044106, 2014.
5. S. Ren, M. Wuttig, and M. Bedzyk, "Epitaxial integration of ferromagnetic and ferroelectric materials," Science, vol. 315, no. 5810, pp. 954-957, 2007.
6. Y. Liu, Y. Wu, D. Li, Y. Zhang, J. Zhang, and J. Yang, "A study of structural, ferroelectric, ferromagnetic, dielectric properties of $NiFe_2O_4$-$BaTiO_3$ multiferroic composites," J. Mater. Sci.: Mater. Electron., vol. 24, no. 6, pp. 1900-1904, 2013.
7. W. Zhang, N. Gao, J. He, C. Shen, D. Wu, and Y. Xie, "Theoretical predictions for magnetoelectric coupling in composite multiferroics with tailored interfaces," Acta Mater., vol. 125, pp. 65-75, 2017.
8. T. Zhang, X. Li, J. Dai, A. Yang, and Y. Tan, "Strain-mediated magnetoelectric coupling in $BiFeO_3$-$NiFe_2O_4$ particulate composites," J. Magn. Magn. Mater., vol. 377, pp. 100-104, 2015.
9. J. Chen, Z. Xu, X. Qu, and Q. Huang, "Preparation and properties of $BiFeO_3$-$CoFe_2O_4$-$PbTiO_3$ multiferroic composite ceramics," J. Alloys Compd., vol. 710, pp. 275-284, 2017.
10. L. Liu, S. Zhang, Y. Wang, Y. Guo, and J. Zhang, "Enhanced magnetoelectric properties of hydrothermally synthesized $BiFeO_3$-$NiFe_2O_4$ composites with controlled interfaces," J. Mater. Chem. C, vol. 6, no. 8, pp. 2076-2086, 2018.
11. Q. Wang, X. Wang, X. Liu, and J. Zhu, "Strain-mediated magnetoelectric effect in particulate compositionally graded $BaTiO_3$-$CoFe_2O_4$ composites," J. Am. Ceram. Soc., vol. 99, no. 7, pp. 2425-2432, 2016.
12. M. Zhou, Y. Li, S. Cai, L. Shan, and X. Liu, "Enhanced magnetoelectric coupling in sol-gel derived 3-1 type multiferroic composites with tailored microstructure," Ceram. Int., vol. 44, no. 1, pp. 4364-4372, 2018.
13. Y. Liu et al., "Hydrothermal synthesis and enhanced magnetoelectric properties of $BiFeO_3$-$NiFe_2O_4$ composites with adjustable

interfaces," J. Mater. Chem. C, vol. 7, no. 3, pp. 764-773, 2019.

14. R.C. Kambale, D.Y. Jeong, and J. Ryu, "Current status of magnetoelectric composite thin/thick films," Adv. Cond. Matter Phys., vol. 2012, p. 824643, 2012.
15. C. Israel, N.D. Mathur, and J.F. Scott, "A one-cent room-temperature magnetoelectric sensor," Nat. Mater., vol. 7, no. 2, pp. 93-94, 2008.
16. J. Ma, J. Hu, Z. Li, and C.W. Nan, "Recent progress in multiferroic magnetoelectric composites: from bulk to thin films," Adv. Mater., vol. 23, no. 9, pp. 1062-1087, 2011.
17. Y. Wang, J. Li, and D. Viehland, "Magnetoelectrics for magnetic sensor applications: status, challenges and perspectives," Mater. Today, vol. 17, no. 6, pp. 269-275, 2014.
18. M. Bibes and A. Barthélémy, "Multiferroics: towards a magnetoelectric memory," Nat. Mater., vol. 7, no. 6, pp. 425-426, 2008.
19. J.F. Scott, "Applications of magnetoelectrics," J. Mater. Chem., vol. 22, no. 11, pp. 4567-4574, 2012.
20. C.W. Nan, M.I. Bichurin, S. Dong, D. Viehland, and G. Srinivasan, "Multiferroic magnetoelectric composites: historical perspective, status, and future directions," J. Appl. Phys., vol. 103, no. 3, p. 031101, 2008.
21. H. Palneedi, V. Annapureddy, S. Priya, and J. Ryu, "Status and perspectives of multiferroic magnetoelectric composite materials and applications," Actuators, vol. 5, no. 1, p. 9, 2016.
22. L. Martin, Y. Chu, and R. Ramesh, "Advances in the growth and characterization of magnetic, ferroelectric, and multiferroic oxide thin films," Mater. Sci. Eng. R, vol. 68, no. 4-6, pp. 89-133, 2010.
23. S. Dong, J. Zhai, J. Li, D. Viehland, and S. Priya, "Multimodal system for harvesting magnetic and mechanical energy," Appl. Phys. Lett., vol. 93, no. 10, p. 103511, 2008.
24. H. Greve et al., "Giant magnetoelectric coefficients in $(Fe_{90}Co_{10})_{78}Si_{12}B_{10}$-AlN thin film composites," Appl. Phys. Lett., vol. 96, no. 18, p. 182501, 2010.
25. Z. Chu et al., "Enhanced resonance magnetoelectric coupling in (1-1) connectivity composites," Adv. Mater., vol. 29, no. 19, p. 1606022, 2017.
26. J. Das, Y.Y. Song, N. Mo, P. Krivosik, and C.E. Patton, "Electric-field-tunable low loss multiferroic ferrimagnetic-ferroelectric heterostructures," Adv. Mater., vol. 21, no. 20, pp. 2045-2049, 2009.
27. P. Record, C. Popov, J. Fletcher, E. Abraham, Z. Huang, H. Chang, and R. Whatmore, "Direct and converse magnetoelectric effect in laminate bonded Terfenol-D-PZT composites," Sens. Actuators B Chem., vol. 126, no. 1, pp. 344-349, 2007.
28. M. Bichurin, V. Petrov, and G. Srinivasan, "Theory of low-frequency magnetoelectric coupling in magnetostrictive-piezoelectric bilayers," Phys. Rev. B, vol. 68, no. 5, p. 054402, 2003.
29. G. Srinivasan, E.T. Rasmussen, J. Gallegos, R. Srinivasan, Y.I. Bokhan, and V.M. Laletin, "Magnetoelectric bilayer and

multilayer structures of magnetostrictive and piezoelectric oxides," Phys. Rev. B, vol. 64, no. 21, p. 214408, 2001.

30. S. Zhao, J.G. Wan, M. Yao, J.M. Liu, F.Q. Song, and G.H. Wang, "Flexible $CoFe_2O_4$-$Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ thin films: integration of ferroelectric and magnetic properties," Adv. Mater., vol. 22, no. 21, pp. 2369-2373, 2010.