Chemical Engineering Journal
Volume 522, 15 October 2025, 167263

Remarkable energy storage performance in lead-free tungsten bronze ferroelectrics for high temperature applications

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Received 9 June 2025, Revised 30 July 2025, Accepted 14 August 2025, Available online 16 August 2025, Version of Record 20 August 2025.

Cite as M.F. Riaz, F. Hussain, A.D. Chandio, Z. Javed, W. Yue, Z. Fan, Y. Du, B. Wang, M.A. Abdeen, G. Abdurakhmanov, A. Alshoaibi, Y. Tabak, A. Evcin, K. Song, D. Wang, Remarkable energy storage performance in lead-free tungsten bronze ferroelectrics for high temperature applications. Chem. Eng. J. **522**, 167263 (2025).

https://doi.org/10.1016/j.cej.2025.167263

Highlights

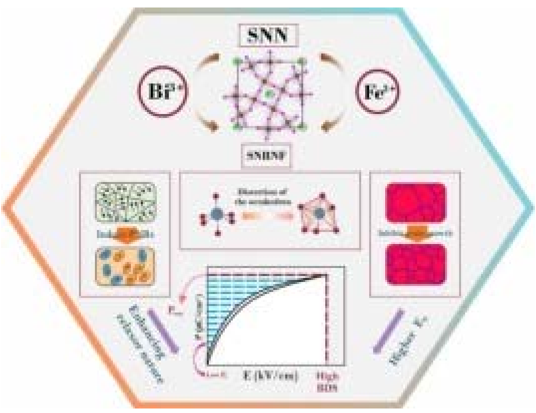
- A series of lead-free $Sr_2NaNb_5O_{15}$ TTB based formulations have been prepared through Bi^{3+} and Fe^{3+} co-doping approach.

- $0.15x$-SNBNF formulation shows record high W_{rec} = 5.23 J/cm^3 with η = 85 % at high electric field (TTB based SNN system).
- Exceptional frequency, fatigue and temp. stability are achieved in terms of both energy storage density and efficiency.
- P_D = 214.3 MW/cm^3, C_D = 2382 A/cm^2, and $t_{0.9}$ = 30 ns reveals its potential application for advanced energy storage devices.

Abstract

Achieving simultaneous optimization of high energy storage density at high temperature and robust stability in tungsten bronze-based ferroelectrics remains challenging for practical capacitor applications. This study presents significant advancement in $Sr_2NaNb_5O_{15}$-based tetragonal tungsten bronze (TTB) ceramics through Bi/Fe co-doping strategy. The developed $Sr_2Na_{(1-x)}Bi_{(x)}Nb_{(5-x)}Fe_{(x)}O_{15}$ (SNBNF) system demonstrates significantly enhanced energy storage performance via structural modification and relaxor behavior optimization. Remarkably, the 0.15×-SNBNF composition achieves a record recoverable energy density (W_{rec}) of 5.23 J/cm^3 with 85 % efficiency at 400 kV/cm, surpassing previous TTB-based systems and rivalling perovskite counterparts. The material exhibits a notable stability with minimal variations in W_{rec} (≤6.5 %) across wide frequency (1–500 Hz), temperature (30–150 °C), and fatigue cycling (10^5 cycles) in ferroelectric testing conditions. Achieving ultrahigh power density (214.3 MW/cm^3), current density (2382 A/cm^2), and ultrafast discharge ($t_{0.9}$ = 30 ns) together in single compound represents promising candidate in lead-free ceramics for advanced high temperature energy storage applications.

Graphical abstract



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Introduction

In recent years, the research and development of novel materials for energy storage have become indispensable for complying with the fundamentals of an environmentally friendly approach [[1], [2], [3], [4]]. In the pulse power domain, dielectric ceramic capacitors, as superior energy storage electrical components, play a crucial character because of their thermal stability [5], rapid charge and discharge energy storage capabilities [[6], [7], [8]], affordability, and additional characteristics [9,10]. The formulas mentioned below are used to calculate the energy storage properties of dielectric materials.

In these equations mentioned above, W_{total} denotes the total energy storage density, W_{rec} represents the recoverable energy storage density, P_{max} denotes the highest saturation polarization, P_r shows the remanent polarization in the material, and η represents the efficiency. Achieving superior W_{rec} and higher η necessitates the integration of elevated breakdown field (E_b), high $P_{max,}$ and low P_r as indicated. The term "dielectric ceramics" may be divided into four distinct categories: linear dielectric materials (LD), normal ferroelectrics (FEs), antiferroelectric (AFEs), and relaxor ferroelectrics (RFEs). For energy storage, it appears that RFEs that possess high dynamic and weaker coupled polar nanoregions (PNRs) are the most suitable materials [11]. Despite this, the weakly coupled PNRs are sensitive to electric fields and react rapidly to changes in the external electric field. Consequently, they acquire a substantial P_m and an insignificant P_r, which will lead to a big ΔP ($P_m - P_r$) and guarantee the accomplishment of tremendous W_{rec} and η in RFEs [12]. Concurrently, the dielectric property of a relaxant typically undergoes a moderate change in response to temperature, which is conducive to obtaining relatively stable dielectric permittivity, ferroelectricity, and energy storage density across a broad range of temperatures [13]. Recent years have witnessed research on tetragonal tungsten bronze ferroelectrics as an alternative to perovskite, owing to their remarkable optoelectronic and pyroelectric properties and outstanding non-linear optics [[14], [15], [16]]. The molecular formula $(A1)_4(A2)_2(B)_{10}O_{30}$, tetragonal tungsten bronze (TTB) structure has engrossing extensive attention in the field of energy storage materials [[17], [18], [19], [20]]. The crystal structure also has octahedral sites with 9-fold oxygen coordination at the C site, 6-fold at the B site, and 15- and 12-fold at the A-2 sites [21]. In addition, the A1-site and A2-site are utilized by various ions such as Sr^{2+}, Ba^{2+}, Pb^{2+}, K^+, Ca^{2+}, Na^+, and a few cations such as Ta^{5+} and Nb^{5+} to occupy the B sites. A few small cations and Li^+ occupy the C sites.

A variety of SNN-based TTB compounds have been investigated for developing a relaxor characteristic and enhancing energy storage capabilities via A/B-site doping [22]. For instance, Feng et al. developed $Sr_3SmNa_2Fe_{0.5}Nb_{9.5}O_{30}$ TTB ceramics that realized (W_{rec} = 1.7 J/cm$^{3)}$ and (η = 80 %) at E = 290 kV/cm [23]. Li et al. fabricated $(Sr_{0.7}Ba_{0.3})_{2-x}Bi_xNaNb_{5-x}Ti_xO_{15}$ ceramics with TTB structure and reported a W_{rec} of 1.8 J/cm^3 along with an efficiency of 87 % at E = 210 kV/cm [22]. W_{rec} = 3.99 J/cm^3 and η = 91.7 % @ 380 kV/cm was achieved in TTB-based $Sr_2NaNb_5O_{15}$ with Ta doping, as reported by Zhang et al. [18]. However, unlike the SBN system, the W_{rec} remains unsatisfactory, not more than 4 J/cm^3, due to the presence of volatile element Na in an SNN-based system [24]. Therefore, substitution in Na at A2-site can be beneficial for improvement in ferroelectric properties. Due to ion doping, the modulation of ferroelectric and relaxor behavior in TTB ceramics is mostly attributed to cation saturation and structural distortions [[25], [26], [27], [28], [29]]. According to the crystal chemical framework, an averaged smaller A-site ionic radius decreases O-B-O bond length, enhancing relaxor

characteristics. The diminished B   O bonding, local structural fluctuations or distortions, and order-disorder distributions all facilitate the alteration of the B-site cation to enhance relaxor nature [30,31]. Various approaches may be employed to modify the relaxor characteristics of TTB ceramics, and their adjustable structures and extensive property tunability offer an appropriate framework for achieving the objective of materials with exceptional energy storage performance [17]. Consequently, the TTB ceramic family merits further investigation and exploration as a medium for energy storage. Furthermore, $BiFeO_3$ (BF) revealed strong polarization, resulting in high ESP when doped in a perovskite structure [32]. However, doping of BF in SNN-based TTB ceramics has never been reported yet.
In the present work, by adopting a co-doping strategy, Bi^{3+} and Fe^{3+} were introduced at A/B sites in the SNN matrix to enhance the relaxor nature and breakdown strength simultaneously. Incorporating Bi^{3+} ions into the A-site of SNN ceramics may enhance polarity (P_{max}) due to $6s^2$ lone pair hybridization with O-2p, while inhibiting grain growth to improve breakdown strength. Additionally, Fe^{3+} substitution at the B-site is expected to distort the BO_6 octahedron, disrupting ferroelectric order and inducing hyper-chaos. Fig. 1 depicts the graphical illustration of the mechanism mentioned above. Eventually, a record high W_{rec} = 5.23 J/cm^3 with η of 85 % is achieved, which is superior to all previous reports on TTB-based SNN systems, owing to decrease in grain size, high relative permittivity, and low dielectric losses. Likewise, high-power density (214.3 MW/cm^3) and ultrafast discharge time ($t_{0.9}$ = 30 ns) additionally enhanced the potential of the SNBNF compound. The effect of Bi^{3+} and Fe^{3+} on the structural, dielectric, and energy storage properties combined with finite element simulation, energy charge-discharge performance, and exceptional character of relaxor behavior were also revealed. This study created a new lead-free preferred material for electronic applications and emphasized the research potential of TTB ceramics for energy storage devices.

Section snippets

Experimental

$Sr_2Na_{(1-x)}Bi_{(x)}Nb_{(5-x)}Fe_{(x)}O_{15}$ (xSNBNF, x = 0, 0.05, 0.10, 0.15, 0.20) ceramics were fabricated via solid-state technique. These ceramics prepared with high-purity chemicals of Aladin are

Nb_2O_5 (≥99.9 %), $SrCO_3$ (≥99.0 %), Fe_2O_3 (≥99.9 %), Na_2CO_3 (≥99.8 %), and Bi_2O_3 (≥99.0 %). After being dried for 24 h at 180 °C, the powdered raw materials were weighed separately using the stoichiometric ratio. To homogenize the ceramic powder, ball milling in ethanol was carried out for 24 h. Followed by ball

Results and discussion

Fig. 2(a) illustrates the XRD patterns of $Sr_2Na_{(1-x)}Bi_{(x)}Nb_{(5-x)}Fe_{(x)}O_{15}$ (xSNBNF) compounds at room temperature. All samples display a singular tetragonal tungsten bronze structure devoid of any secondary phase, JCPDS No. 34–0429, with a space group of P4bm, as examined by MDI Jade using XRD raw data, signifying that Bi^{3+} and Fe^{3+} are entirely incorporated into the primary lattice of SNN based compound. Fig. 2(b) presents an enhanced illustration of the diffraction patterns for the ceramics

Conclusions

Lead-free SNN-based $Sr_2Na_{(1-x)}Bi_{(x)}Nb_{(5-x)}Fe_{(x)}O_{15}$ ceramics with superior properties were produced to analyze the effect of substitution at A/B sites for high temperature applications. The structural analysis sanctions the formation of a single-phase tetragonal tungsten bronze structure without any secondary phase. The AGS also shows a declining trend with increasing doping content, as revealed through microstructural investigation. Taking advantage of the refined grains and polar nano regions

CRediT authorship contribution statement

Muhammad Fahad Riaz: Writing – original draft, Investigation, Data curation. **Fayaz Hussain:** Writing – review & editing, Supervision, Project administration. **Ali Dad Chandio:** Writing – review & editing, Supervision. **Zeshan Javed:** Writing – review & editing, Investigation, Conceptualization. **Wenfeng Yue:** Methodology. **Zhenhao Fan:** Formal analysis. **Yuxiao Du:** Writing – review & editing. **Bingsen Wang:** Writing – review & editing. **Mohammad Abu Abdeen:** Writing – review & editing. **Gulmurza Abdurakhmanov:**

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research work is mainly supported for PhD by the Materials Engineering Department, NED University of Engineering & Technology, Karachi. Authors are very thankful to the Department of Instrumentation Science & Engineering, Harbin Institute of Technology (HIT), China, for advanced characterization and fabrication of samples for further study. The authors are truly grateful to the Higher Education Commission of Pakistan for funding under Faculty Development Program and HEC (NRPU-17049 Grant).

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