

$\text{Sr}_{1-x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ 固溶体系陶瓷的结构与电性能

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摘 要: 从 SrNb_2O_6 - NaNbO_3 的二元固溶相图出发, 通过传统固相法合成了一系列 $\text{Sr}_{1-x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ (SNN, $0.56 \leq x \leq 1.06$) 陶瓷材料, 通过 X 射线衍射、扫描电子显微镜和电性能实验, 研究了第二相对 SNN 陶瓷结构、介电、铁电性能的影响并确定了 SNN 纯相的组成条件和温度范围。结果表明: 当 $x = 0.71 \sim 0.80$ 时, 陶瓷在 $1200 \sim 1360^\circ\text{C}$ 范围内可获得稳定的纯相, 且 SNN 纯相的存在取决于陶瓷的组成和烧结温度。当 $x = 0.71 \sim 0.88$ 范围内时, SNN 陶瓷的电学性能相对较好, $x = 0.80$ 的陶瓷表现出优异的铁电性能: $P_r = 11.49 \mu\text{C}/\text{cm}^2$, $E_c = 20.99 \text{KV}/\text{cm}$ 。

关键词: 铌酸锶-铌酸钠二元固溶体; 陶瓷组分; 烧结温度; 铁电性能
中图分类号: TQ174.75 文献标志码: A 文章编号: 0454-5648(2026)06-1980-11
网络出版时间: 2026-05-13



1 Introduction

As an important branch of lead-free piezoelectric materials, ceramics with the tetragonal tungsten bronze (TTB) structure have a high spontaneous polarization strength, high Curie temperature (T_C), and beneficial dielectric properties, making them particularly useful in ferroelectric applications^[1,2]. The general formula of TTB ceramics is given as $(\text{A}1)_4(\text{A}2)_2\text{C}_4(\text{B}1)_2(\text{B}2)_8\text{O}_{30}$, which is composed of corner-connecting BO_6 octahedra that create three kinds of channels: 15-coordinated pentagonal A1-sites, 12-coordinated square A2-sites, and 9-coordinated triangular C-sites (see Fig. 1). In general, A1- and A2-sites are occupied by univalent alkaline metal ions with larger radii, such as K^+ and Na^+ , and divalent alkaline earth metal ions, such as Sr^{2+} , Ba^{2+} , and Ca^{2+} , as well as trivalent rare earth metal ions, such as La^{3+} , Nd^{3+} , Eu^{3+} ; the relatively small C-sites are occupied by cations with smaller radii, such as Li^+ , Be^{2+} , and Mg^{2+} ;

whereas the B1- and B2-sites in the center of oxygen octahedra are occupied by transition metal cations with a high valence, such as Nb^{5+} , Ta^{5+} , and Sb^{5+} ^[3,4]. In TTB compounds, the interactions between

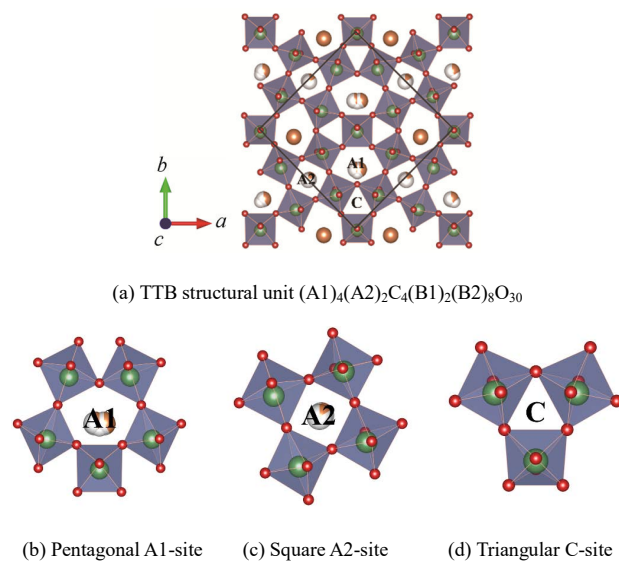


Fig. 1 Schematic diagrams of TTB structural unit and different sites projected in the $[001]$ direction

收稿日期: 2025-09-24。 修订日期: 2026-02-04。

基金项目: 国家自然科学基金面上项目(22475125); 陕西省教育厅科学研究计划(24JK0709); 陕西省科技厅自然科学基金基础研究计划(2025JC-YBQN-503); 咸阳师范学院科研计划(XSYK24029)。

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Received date: 2025-09-24.

Revised date: 2026-02-04.

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B atoms and the O octahedral frame in the BO_6 octahedral polar unit significantly affect the dielectric and ferroelectric properties, which can easily be adjusted by employing various cation substitutions at the A-sites^[5,6].

Depending on which sites are filled, the TTB structure can be divided into three categories: the “stuffed” structure, where all the cation sites are occupied; the “filled” structure, where the A-sites are all filled but the C-sites are half or all empty; and the “unfilled” structure, where the A-sites are partially filled and the C-sites are all empty^[7,8]. Therefore, TTB compounds can be regulated through compositional design to exhibit a wide range of structures and functional characteristics, which have broad development potential in the fields of dielectric energy storage, multiferroic materials, nonlinear optics, and pyroelectric sensors^[9–12].

As a typical “filled” TTB compound, $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (SNN) ceramics have been extensively studied in recent years^[13,14]. However, SNN ceramics require relatively high sintering temperatures, and the secondary phase $\text{Na}_{0.5}\text{Sr}_{0.25}\text{NbO}_3$ (NSN) readily forms during the sintering process, which adversely affects the electrical properties^[15–17]. Zhang *et al.*^[18] found that atmosphere sintering can inhibit the formation of Na and O vacancies caused by Na_2O volatilization during sintering, thereby improving the densification and electrical properties of SNN ceramics. Furthermore, lower sintering temperatures were achieved, compared with those required in the traditional high-temperature solid-state method. Subsequently, Zhang *et al.*^[19] prepared dense ceramics with a controllable Sr/Na ratio by leveraging atmosphere sintering and sol-gel processing techniques. In our previous work^[20,21], Ag^+ doping eliminated the NSN impurities in SNN ceramics and improved the electrical performance. We also found that Bi^{3+} doping helped enhance the densification and electrical performance of SNN ceramics, and the impurity phase concurrently disappeared because the filling degree of the A1- and A2-sites decreased.

Although some studies have discussed the methods of eliminating the impurity phase, there are

few studies on the relationship between impurities and the properties of SNN ceramics. Notably, Sr^{2+} and Na^+ are disordered at the A1- and A2-sites, and the NbO_6 octahedra at the B-sites act as polarization units; thus, every factor that can affect the environment around the NbO_6 octahedron has the potential to change the properties. In the present work, SNN ceramics (*i.e.*, $\text{Sr}_{1-x}\text{Na}_x\text{Nb}_5\text{O}_{15}$, $0.56 \leq x \leq 1.06$) were prepared *via* traditional solid-state reactions from the SrNb_2O_6 (SN)- NaNbO_3 (NN) binary solid solution system, to examine the relationship between the presence of the secondary phases and the ceramic composition, as well as the sintering temperature. Ultimately, the required composition and sintering temperature ranges of the SNN pure phase are determined, and the influences of the secondary phases on the structure and electrical properties are discussed. Considering the binary solid solution phase diagram^[22], Table 1 shows the NaNbO_3 molar fraction, structural formula (corresponding simple expression), and filling degree of the SNN ceramics evaluated in this paper.

Table 1 Filling degree of the SNN structure with different molar fraction(x) of NaNbO_3

$x(\text{NaNbO}_3)/\%$	Structural formula	Filling degree
20.0	$\text{Sr}_{2.22}\text{Na}_{0.56}\text{Nb}_5\text{O}_{15}$ ($x = 0.56$)	$(2.22+0.56)/3 = 0.927$
22.5	$\text{Sr}_{2.18}\text{Na}_{0.63}\text{Nb}_5\text{O}_{15}$ ($x = 0.63$)	$(2.18+0.63)/3 = 0.937$
24.0	$\text{Sr}_{2.16}\text{Na}_{0.68}\text{Nb}_5\text{O}_{15}$ ($x = 0.68$)	$(2.16+0.68)/3 = 0.947$
25.0	$\text{Sr}_{2.14}\text{Na}_{0.71}\text{Nb}_5\text{O}_{15}$ ($x = 0.71$)	$(2.14+0.71)/3 = 0.95$
27.5	$\text{Sr}_{2.10}\text{Na}_{0.80}\text{Nb}_5\text{O}_{15}$ ($x = 0.80$)	$(2.10+0.80)/3 = 0.967$
30.0	$\text{Sr}_{2.06}\text{Na}_{0.88}\text{Nb}_5\text{O}_{15}$ ($x = 0.88$)	$(2.06+0.88)/3 = 0.98$
33.3	$\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ ($x = 1.00$)	$(2.00+1.00)/3 = 1.00$
35.0	$\text{Sr}_{1.97}\text{Na}_{1.06}\text{Nb}_5\text{O}_{15}$ ($x = 1.06$)	$(1.97+1.06)/3 = 1.01$

2 Experimental procedures

SNN ceramics ($\text{Sr}_{1-x}\text{Na}_x\text{Nb}_5\text{O}_{15}$, $0.56 \leq x \leq 1.06$) were synthesized using polycrystalline SN and NN; accordingly, these powders were synthesized first. SN and NN powders were prepared using the solid-state method, employing reagent-grade SrCO_3 (99.99%), Na_2CO_3 (99.99%), and Nb_2O_5 (99.99%) as the raw materials. The starting materials were pre-dried at 120 °C for 24 h, and then weighed according to the target stoichiometric ratios. The

powders were thoroughly mixed in ethanol using ZrO_2 balls in a planetary ball mill at 401 r/min for 20 h. The mixtures were dried at 80 °C for 24 h, and then the SN mixture was calcined at 1100 °C for 4 h, whereas the NN mixture was calcined at 800 °C for 3 h. Subsequently, the SN and NN powders were obtained by separately grinding the calcined products in a mortar after natural cooling. Next, the SN and NN powders were mixed according to the desired SNN compositions, calcined at 1220 °C for 6 h, and uniaxially compacted into pellets with a binder, namely 5% (in mass) polyvinyl alcohol; the binder was removed by applying high temperature. Finally, considering the melting points of SN and NN, SNN ceramics were prepared by sintering at 1280–1340 °C for 4 h.

The phase structures of the obtained powders and ceramics were examined at room temperature *via* powder X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation (D8 Advance, Bruker, Germany) with a step size of 0.02° and a 2θ range of 20°–60°. The sample microstructures were observed *via* Tungsten filament scanning electron microscopy (SEM; SU3500, Hitachi High-tech Company). The field emission transmission electron microscope (FE-TEM, Thermo Fisher Talos-F200X) was utilized to acquire the atomic resolution high angle annular dark field (HAADF) and the selected-area electron diffraction (SAED) patterns. Furthermore, the ceramics were ground and polished down to a thickness of about 0.6 mm, coated with silver electrodes, and fired at 840 °C for 30 min, and then their dielectric characteristics were evaluated from –200 °C to 200 °C using an LCR HiTESTER (Hioki 3532-50) at a heating rate of 2 °C/min and from room temperature to 500 °C using an LCR meter (Agilent E4980A, Palo Alto, CA), also at a heating rate of 2 °C/min. The ceramics were also ground and polished down to a thickness of about 0.2 mm and coated with gold electrodes to record the room-temperature ferroelectric hysteresis loops (P – E) at 1 Hz in silicon oil using a Radiant Precision Workstation (Albuquerque, New Mexico, USA); the applied voltage was gradually increased from 10 kV/cm to the breakdown electric field. Finally, the

piezoelectric coefficient d_{33} was measured by a quasi-static piezoelectric meter (ZJ-3d, Institute of Acoustics Academic Sinica, Beijing, China).

3 Results and discussion

Fig. 2 shows the XRD spectra of the as-obtained SN and NN powders in the 2θ range of 20°–60°. Based on JCPDS 28–1243 and JCPDS 33–1270, pure phases were obtained for both powders.

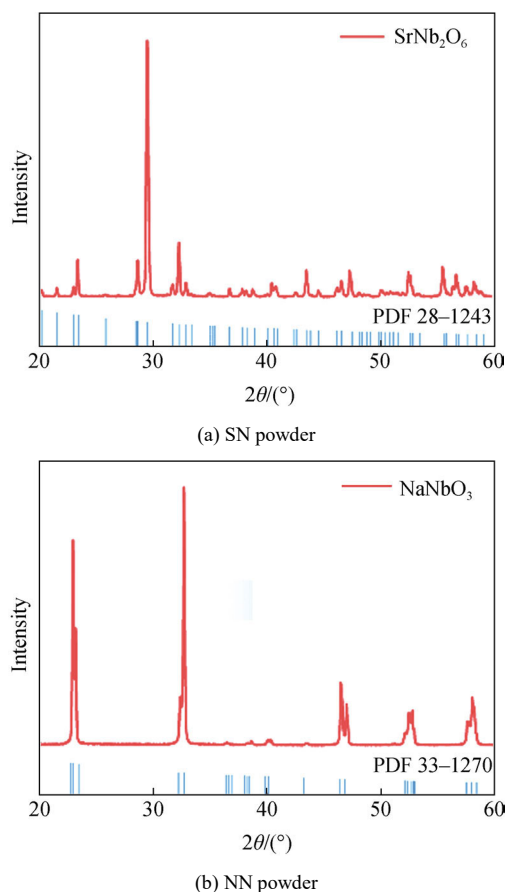


Fig. 2 XRD spectra of the SN and NN powders

Fig. 3a depicts the XRD patterns of the SNN powders calcined at 1220 °C in the 2θ range of 20°–60°, and Fig. 3b shows an enlarged view of Fig. 3a in the 2θ range of 20°–35°. Based on JCPDS 34–0429, when $x = 0.71$ – 0.88 , all ceramics exhibit the pure TTB phase. However, at lower Na^+ contents of $x = 0.56$ – 0.68 , a secondary phase of SN appears and is indexed using JCPDS 28–1243; at higher Na^+ contents of $x = 1.00$ and 1.06 , a secondary phase of NN appears and is indexed by JCPDS 33–1270. There exists a small amount of SN or NN when $x = 0.56, 0.63, 0.68$,

1.00, and 1.06 because the SN-NN binary system exceeds the solution limit. Furthermore, as x increases from 0.56 to 0.71, the XRD peak of the SN impurity gradually weakens and disappears. When x reaches 1.00, the NN impurity appears, and the peak intensity gradually enhances as x further increases. Ultimately, the pure TTB phase can be obtained at a calcining temperature of 1220 °C when $x = 0.71$ –0.88, for which

the diffraction peaks can be indexed by JCPDS 34–0429.

Fig. 4a depicts the XRD patterns of the SNN ceramics sintered at 1340 °C in the 2θ range of 20°–60°. All diffraction peaks can be indexed by JCPDS 34–0429 (space group $P4bm$), and no secondary phase is observed when $x = 0.56$ –0.80, indicating that the SN-NN binary system can be

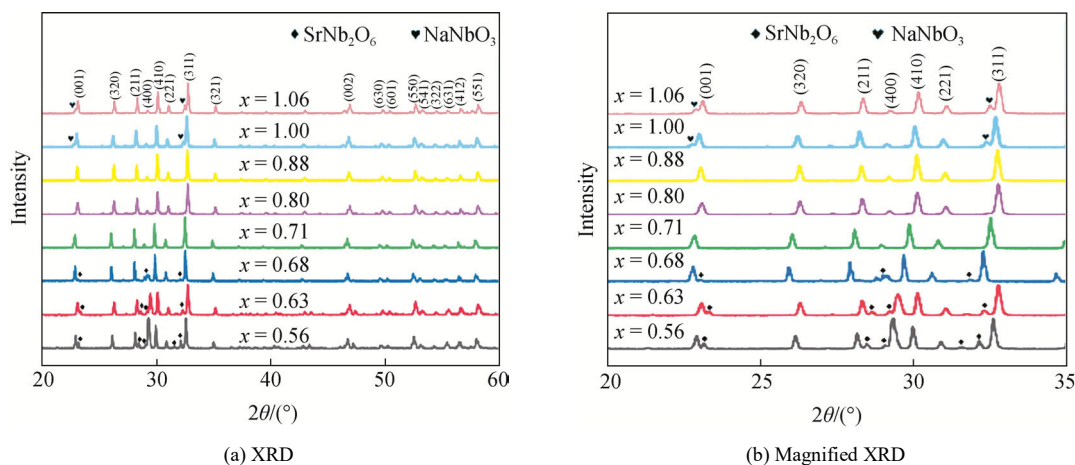


Fig. 3 XRD patterns and locally magnified peaks of the SNN powders calcined at 1220 °C

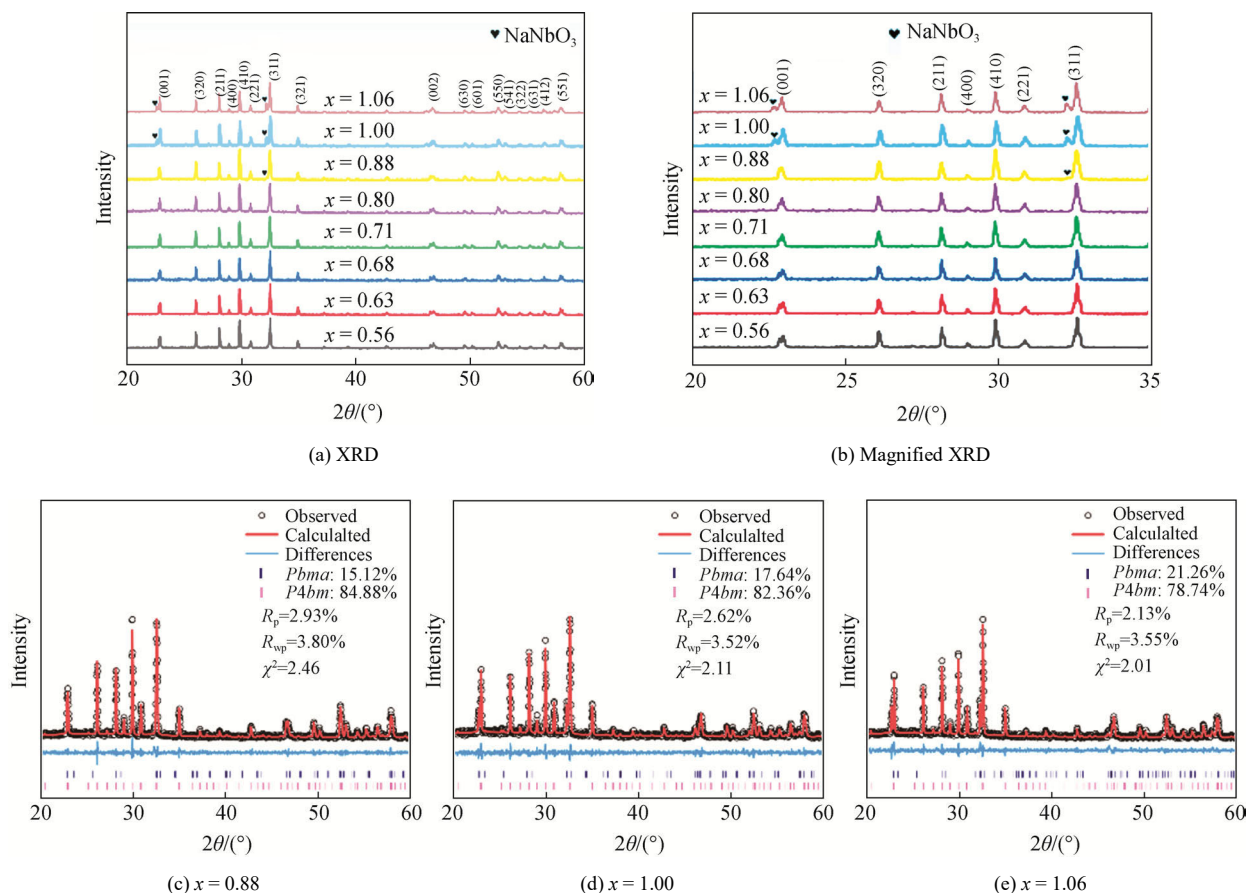


Fig. 4 XRD patterns, locally magnified peaks, and Rietveld refinements of the SNN ceramics sintered at 1340 °C

dissolved in the solid solution at the sintering temperature of 1340 °C. When $x > 0.80$, the pure phase cannot be obtained, and the secondary phase NN appears, indexed by JCPDS 33–1270 (space group *Pbma*). As x continues to increase, the NN peak intensity increases, which is confirmed by the enlarged spectra for the 2θ range of 20°–35° in Fig. 4b. The refinement results for $x = 0.88$, 1.00, and 1.06 are shown in Figs. 4c–4e, and their XRD patterns are refined with orthogonal (*Pbma*) and tetragonal (*P4bm*) structures, confirming the secondary phase NN exists with refinement reliability of R_p and $R_{wp} < 5\%$ (Table S1 in the supplementary material). With a further increase in x , the proportion of the secondary phase NN gradually rises to 15.12%, 17.64% and 21.26%, which is consistent with the results in Fig. 4b.

The XRD patterns of the SNN powders and ceramics were comprehensively analyzed. When $x = 0.56$ –0.68, they can be solidly dissolved at 1340 °C but not at 1220 °C; when $x = 0.71$ –0.80, the stable, pure TTB phase can be obtained from 1220 to 1340 °C; when $x = 1.00$ –1.06, the pure phase cannot form between 1220 and 1340 °C. However, a special circumstance arises when $x = 0.88$: the pure phase was obtained at 1220 °C, but the secondary NN phase was observed at 1340 °C, owing to the decomposition of SNN at higher temperatures. Hence, the presence of the SNN pure phase depends on both the composition and sintering temperature.

A detailed relationship between the phase structure and composition, as well as the temperature of SNN ceramics, was observed under a wide sintering temperature range of 1200–1360 °C, and the results are displayed in Fig. 5. For Na^+ contents of $x = 0.56$ –0.68, SN-NN can be solidly dissolved to obtain a pure phase at high temperatures (> 1280 °C). With the increase to $x = 0.71$ and 0.80, SN-NN can be solidly dissolved throughout the temperature range of 1200–1360 °C. When the Na^+ content increases to 0.88, the SN-NN solid solution can be obtained, but it decomposes at higher temperatures (> 1320 °C), accompanying the formation of the secondary NN phase. As the Na^+ content further increases, it cannot be solidly dissolved in the temperature range of 1200–1360 °C.

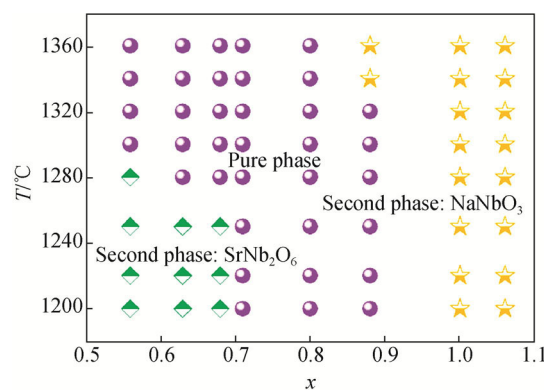


Fig. 5 Phase structure of SNN ceramics in relation to composition and temperature

To discuss the findings in terms of the filling degree, Fig. 6 shows a schematic diagram of the TTB structural unit $(\text{A}1)_4(\text{A}2)_2\text{C}_4(\text{B}1)_2(\text{B}2)_8\text{O}_{30}$ projected in the [001] direction, labeled with pentagonal A1-, square A2-, and triangular C-sites. In the SNN structure, it is widely accepted that Sr^{2+} (1.44 Å) and Na^+ (1.39 Å) are randomly distributed at the A1- and A2-sites because of their similar radii; this disorder of the A-site ions generally causes low-temperature relaxation of the ceramics; the C-sites are not occupied in the SNN structure because they are very small and only small radius ions can enter. According to the chemical formula of $(\text{A}1)_4(\text{A}2)_2\text{C}_4(\text{B}1)_2(\text{B}2)_8\text{O}_{30}$, four A1-sites and two A2-sites can be randomly occupied by Sr^{2+} and Na^+ in the SNN structure. As a result, the SNN ceramics can be induced to exhibit different structural and functional characteristics by regulating the filling degree of the A-site ions.

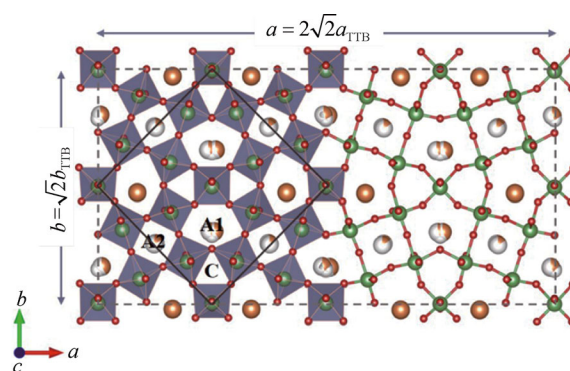


Fig. 6 Schematic diagram of TTB structural unit $(\text{A}1)_4(\text{A}2)_2\text{C}_4(\text{B}1)_2(\text{B}2)_8\text{O}_{30}$ projected in [001] direction

To elucidate the connection between density and sintering temperature, density measurements were

performed for each sample composition prepared at 1200–1360 °C using Archimedes' principle, as presented in Fig. 7. The densities of the ceramics initially increase as the sintering temperature increases, but they slightly decrease after peaking around 1340 °C. Similarly, the densities initially increase as x increases, peaking around $x = 0.68$ and then decreasing. Overall, the maximum density was obtained for samples sintered at 1340 °C, and the densities of all ceramics remained above 4.900 g/cm³ using this sintering temperature.

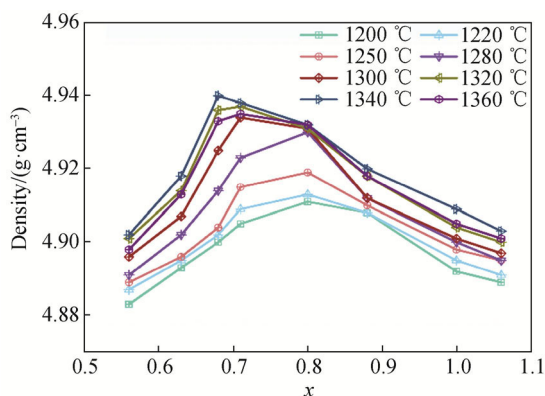


Fig. 7 Densities of the SNN ceramics sintered at different temperatures

Fig. 8a shows the surface morphology of the SNN ceramics sintered at 1340 °C. The prepared ceramics have comparatively dense microstructures and distinct boundaries, with no holes or cracks. In all samples, most grains show an anisometric rod-like shape, which is common for the TTB structure because elongation along the c -axis is easier and faster than in other directions, owing to the lower surface energy^[23,24]. Meanwhile, no significant change in the grain size or growth behavior is observed as x increases, although grain refinement occurs for $x = 0.88$ and 1.00, which is characterized by the increase in equiaxed grains and the suppression of grain size presented, as seen in Fig. 8b.

To further confirm the secondary phase exists in SNN ceramics sintered at 1340 °C when $x > 0.8$, detailed structural analyses were performed using TEM at ambient temperature. Fig. 9a displays an atomic-resolution HAADF image for the ceramic sample with $x = 1.00$. According to the imaging principle, the contrast is proportional to the square of

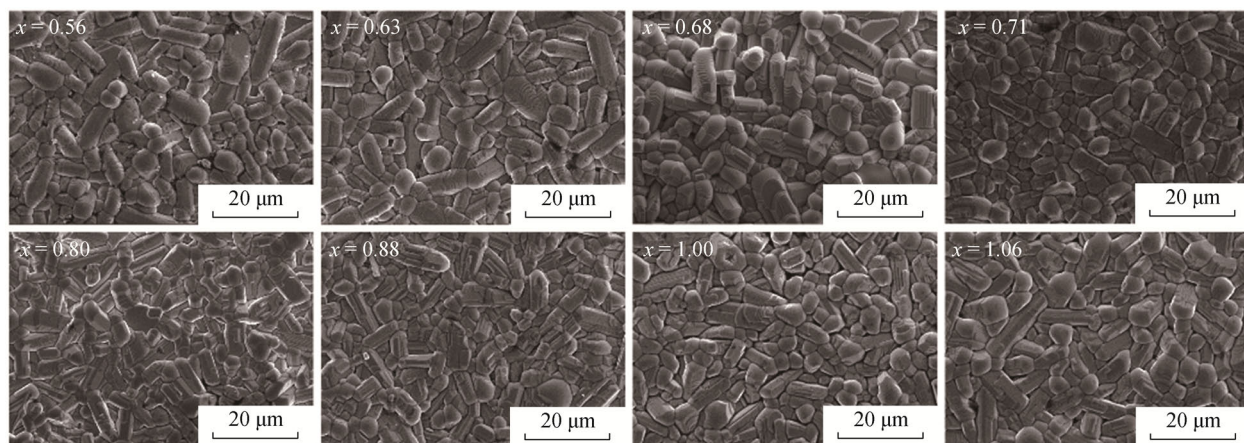
the average atomic number of the imaging area, indicating the secondary phase pointed by the arrow has a relatively low average atomic number. Figs. 9b and 9c show the SAED patterns of the region indicated by the arrow, which can be well indexed based on the basic structure of orthogonal NN, demonstrating the presence of a secondary phase with the orthogonal NN basic structure in the sample, which is in accordance with the results in XRD.

Fig. 10 illustrates the low-temperature (−150–100 °C) and high-temperature (100–500 °C) dependences of the dielectric constant (ϵ) and dielectric loss ($\tan\delta$) for SNN ceramics sintered at 1340 °C, measured at frequencies of 1, 10 kHz and 100 kHz. The ceramics show a small, broad peak below 0 °C, as shown in Figs. 10a–10c, which is believed to be a ferroelastic–ferroelectric phase transition from a $mm2$ phase to a $4mm$ phase^[25]; the temperature corresponding to this peak is T_s , and the corresponding dielectric constant is ϵ_s . This low-temperature dielectric anomaly shows relaxor characteristics, where T_s shifts to higher values as the frequency increases, and ϵ_s decreases correspondingly. The peak can be affected by multiple factors^[26,27], including the ordered–disordered distribution of A-site ions, changes in the crystal microstructure, and the degree of NbO_6 octahedron distortion. For SNN ceramics, the structure changes from “unfilled” to “filled” as the Na^+ content increases, thus weakening the low-temperature relaxor behavior. With increasing temperature, all the ceramic structures convert from a $4mm$ ferroelectric phase to a $4/mmm$ paraelectric phase near 300 °C, as seen in Figs. 10d–10f. This peak corresponds to T_C , and the permittivity is ϵ_m ^[28]. We found that ceramic samples show a certain frequency dispersion, especially $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$. The dielectric loss significantly increases when the temperature approaches T_C , which is mainly due to the scattering of charge carriers during the thermal movement and the leakage loss caused by defects in the crystal^[29].

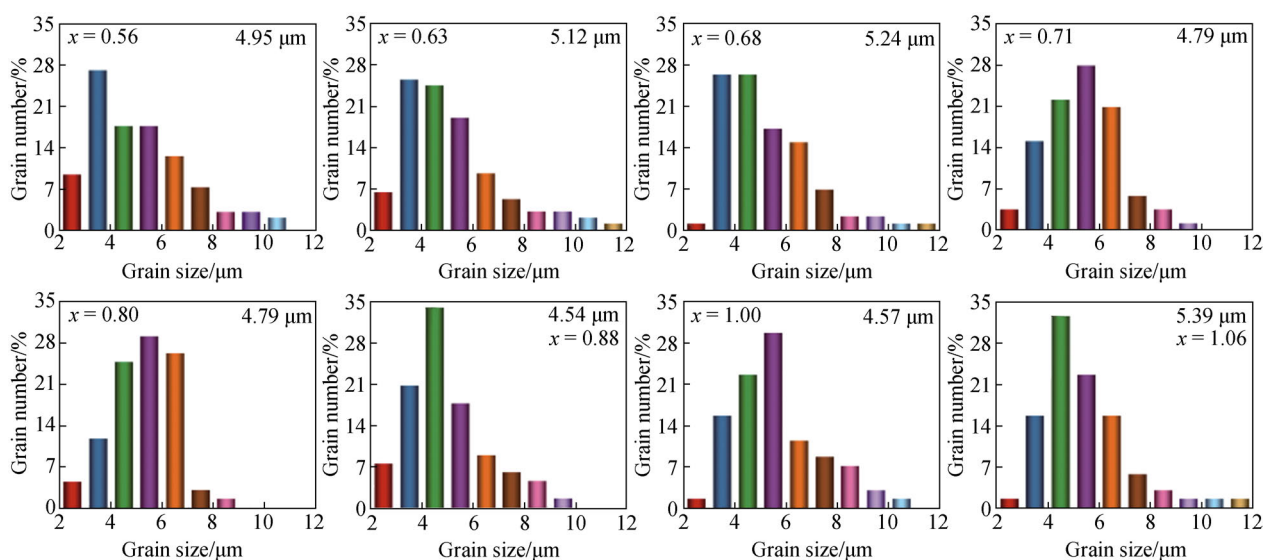
Fig. 11a shows the temperature dependence of ϵ_r and $\tan\delta$ (from −150 °C to 450 °C, measured at 1 kHz) for SNN ceramics sintered at 1340 °C. To further describe the effects of Na^+ content on the dielectric

properties, Fig. 11b shows the variations in ε_m and T_C as a function of x , measured at 1 kHz. Here, T_C increases from 272 °C at $x = 0.56$ to 323 °C at $x = 0.88$ and then gradually decreases; ε_m gradually increases from 1183 to 2141 as x increases from 0.56 to 1.06. T_C increases from

272 °C to 323 °C because the crystal structure changes from “unfilled” to “filled” as the Na^+ content increases, thereby influencing the degree of crystal distortion. However, a minor amount of NN appears when x reaches 0.88, and the amount increases as the Na^+

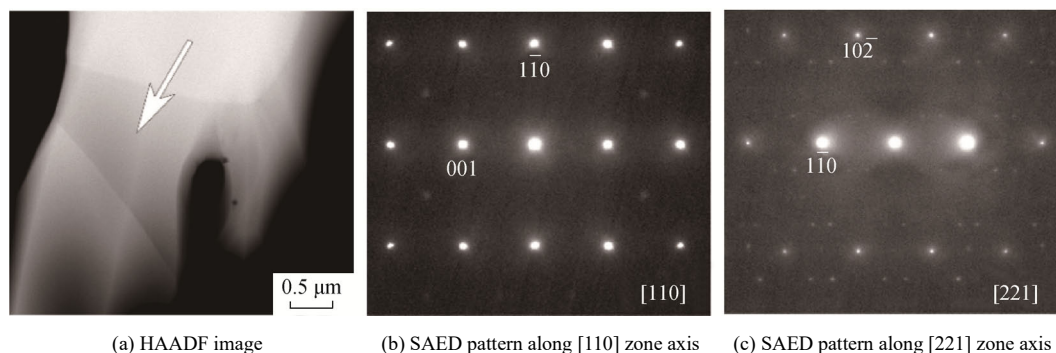


(a) SEM images of the SNN ceramics



(b) Grain size distributions of the SNN ceramics

Fig. 8 Surface morphology of the SNN ceramics



(a) HAADF image

(b) SAED pattern along [110] zone axis

(c) SAED pattern along [221] zone axis

Fig. 9 HAADF image and corresponding SAED patterns of the $x = 1.00$ ceramic

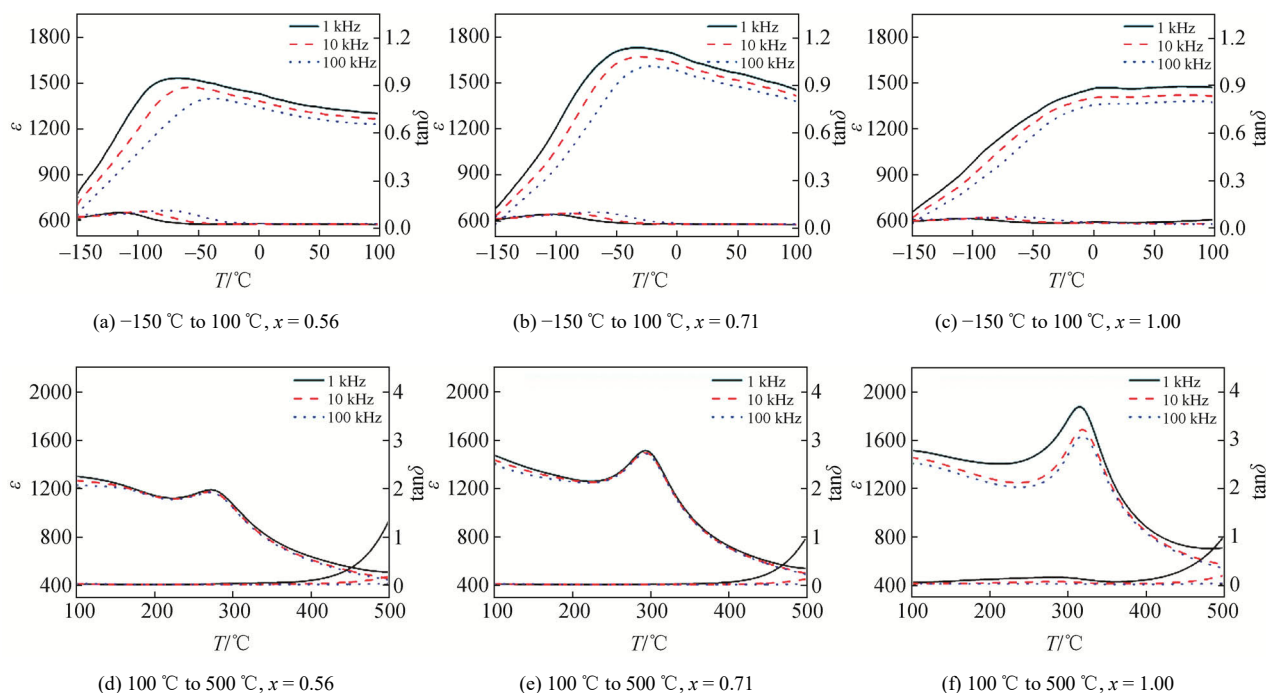


Fig. 10 Temperature dependence of dielectric constant and dielectric loss for the SNN ceramics

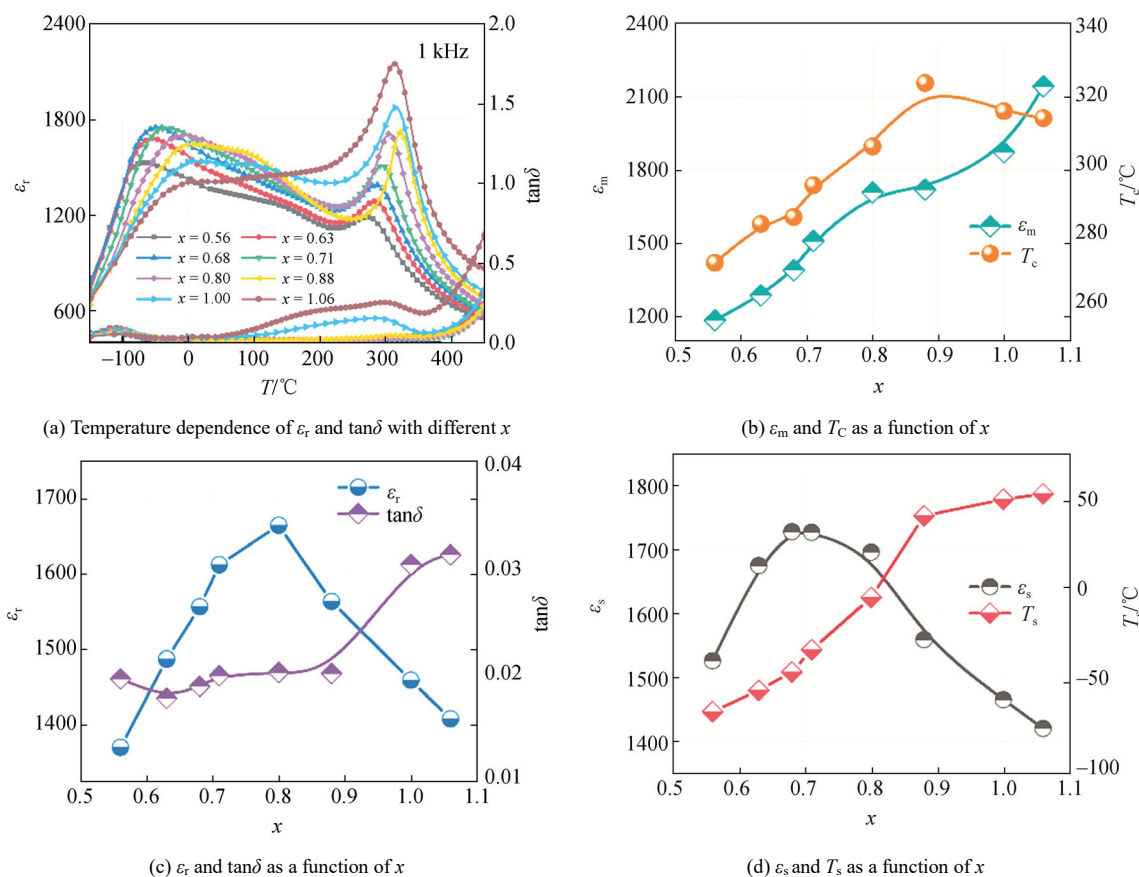


Fig. 11 Dielectric properties of the SNN ceramics

content continues to increase, causing T_c to decrease^[30]. Fig. 11c shows the variations in ϵ_r and $\tan\delta$ as a function

of x , measured at 1 kHz. With increasing Na^+ content, ϵ_r initially increases and then decreases, exhibiting a

maximum of 1664 at $x = 0.80$; $\tan\delta$ remains at a low value at this point. Fig. 11d shows the variations in ϵ_s and T_s as a function of x , measured at 1 kHz. T_s gradually increases from -66.4°C at $x = 0.56$ to 53°C at $x = 1.06$, while ϵ_s increases from 1526 at $x = 0.56$ to 1728 at $x = 0.68$ and then gradually decreases. Therefore, the dielectric properties of SNN ceramics are relatively improved when $x = 0.71$ – 0.88 .

Fig. 12a displays the bipolar P – E hysteresis loops measured at room temperature, for the SNN ceramics sintered at 1340°C . All samples have well-saturated P – E loops, demonstrating ferroelectric behavior, consistent with the domain structure and long-range ferroelectric order^[31]. Fig. 12b illustrates the remnant polarization (P_r) and coercive field (E_c) of the ceramics as a function of x , measured at room temperature. Notably, with increasing Na^+ content, P_r and E_c initially rise and then fall. The P_r ($11.49\ \mu\text{C}/\text{cm}^2$)

and E_c ($20.99\ \text{kV}/\text{cm}$) values are both nearly maximized at $x = 0.80$, yielding the optimal ferroelectric properties for these SNN ceramics. The filling degree of the A-site vacancy increases as the Na^+ content increases, the TTB structure changes from “unfilled” to “filled,” and the ferroelectric performance is enhanced accordingly. However, P_r and E_c decrease when the Na^+ content is too high (*i.e.*, beyond the solution limit of the SN–NN binary system), resulting in the emergence of NN impurities^[32]. The piezoelectric properties are considered to be closely related to ferroelectric performance of the ceramic. The illustration in Fig. 12b shows the piezoelectric constant (d_{33}) of the ceramics as a function of x . According to the graph, the maximum d_{33} value of $34\ \text{pC}/\text{N}$ is obtained for SNN ceramics when $x = 0.80$, which is consistent with the optimal composition for ferroelectric properties.

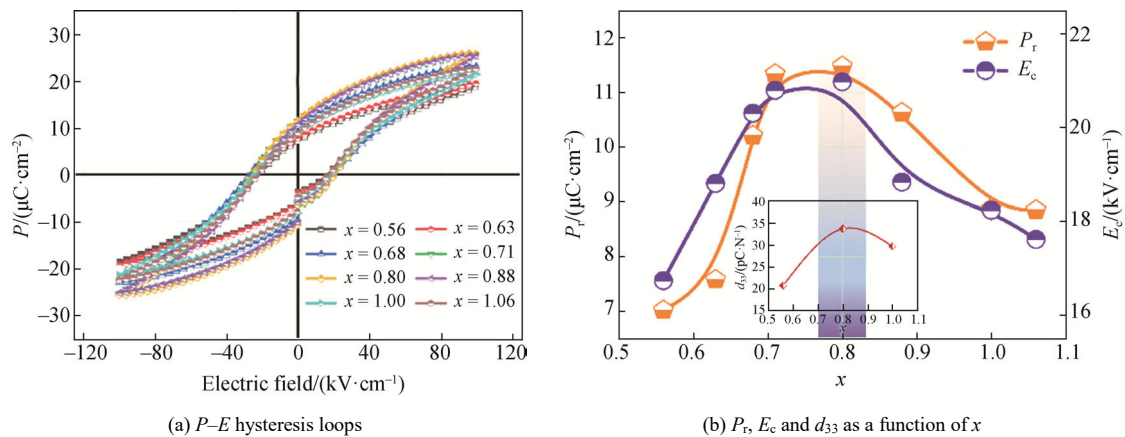


Fig. 12 Ferroelectric and piezoelectric properties of the SNN ceramics

4 Conclusion

Lead-free SNN ($\text{Sr}_{1-x}\text{Na}_x\text{Nb}_5\text{O}_{15}$, $0.56 \leq x \leq 1.06$) ceramics were synthesized using the traditional solid-state method. We found that the dielectric and ferroelectric properties of the SNN ceramics are optimal when $x = 0.71$ – 0.88 . Based on the XRD patterns, ceramics with a stable, pure TTB phase can be obtained from 1200°C to 1360°C when $x = 0.71$ – 0.80 , and the presence of the pure phase depends on both the composition and the sintering temperature. As the Na^+ content increases, T_c initially increases because the filling degree of the TTB structure

increases, and then gradually decreases when $x > 0.88$ because the increase in Na^+ content induces the formation of the secondary NN phase. Furthermore, the SNN ceramic with $x = 0.80$ demonstrates good ferroelectric characteristics (*i.e.*, $P_r = 11.49\ \mu\text{C}/\text{cm}^2$ and $E_c = 20.99\ \text{kV}/\text{cm}$), as determined from the P – E hysteresis loops.

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作者贡献声明:

郝蕊: 论文构思、撰写初稿

邓卓: 设计研究方法和实验方案

马占营: 提供资源、获取资助

于天淼: 数据管理、分析/综合数据并得出结论

曹梦馨: 验证、绘制图表

魏灵灵: 监督指导、审阅与修订

Structure and Electrical Properties of $\text{Sr}_{1-x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ Solid Solution Ceramic Systems

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Extended Abstract

Introduction As an important branch of lead-free piezoelectric materials, ceramics with a tetragonal tungsten bronze (TTB) structure have a high spontaneous polarization strength, high Curie temperature (T_c), and beneficial dielectric properties, making them particularly useful in ferroelectric applications. Depending on which sites are filled, the TTB structure can be divided into three categories, *i.e.*, the “stuffed” structure, the “filled” structure and the “unfilled” structure. As a typical “filled” TTB compound, the $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ (SNN) ceramics can be regulated through compositional design to exhibit a wide range of structures and functional characteristics, which have a broad development potential in the fields of dielectric energy storage, multiferroic materials, nonlinear optics, and pyroelectric sensors. However, SNN ceramics require relatively high sintering temperatures, and the secondary phase $\text{Na}_{0.5}\text{Sr}_{0.25}\text{NbO}_3$ (NSN) readily forms during the sintering process, which adversely affects the electrical properties. Although some previous studies used the methods of eliminating the impurity phase, there could be few studies on the relationship between impurities and the properties of SNN ceramics. In this paper, SNN ceramics (*i.e.*, $\text{Sr}_{1-x}\text{Na}_x\text{Nb}_5\text{O}_{15}$, $0.56 \leq x \leq 1.06$) were prepared with the SrNb_2O_6 (SN)– NaNbO_3 (NN) binary solid solution system, to examine the relationship among the presence of the secondary phases and the ceramic composition, as well as the sintering temperature.

Methods SN and NN powders were synthesized by a solid-state method with reagent-grade SrCO_3 (99.99%), Na_2CO_3 (99.99%), and Nb_2O_5 (99.99%) as raw materials. The starting raw materials were pre-dried at 120 °C for 24 h, and then weighed according to the target stoichiometric ratios. The powders were thoroughly mixed in ethanol in a planetary ball mill with ZrO_2 balls at 401 r/min for 20 h. The mixtures were dried at 80 °C for 24 h, and then calcined at their respective suitable temperatures. Subsequently, the SN and NN powders were obtained by separately grinding the calcined products in a mortar after natural cooling. Afterwards, SNN ceramics ($\text{Sr}_{1-x}\text{Na}_x\text{Nb}_5\text{O}_{15}$, $0.56 \leq x \leq 1.06$) were synthesized with polycrystalline SN and NN according to the desired SNN compositions, calcined at 1220 °C for 6 h, and uniaxially compacted into pellets with a binder (namely 5% polyvinyl alcohol). The binder was removed at a high temperature. Finally, SNN ceramics were prepared by sintering at 1280–1340 °C for 4 h.

The effect of the secondary phases on the structure of SNN ceramics was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and field emission transmission electron microscopy (FETEM). Furthermore, the ceramics were ground and polished down to a thickness of about 0.6 mm, coated with silver electrodes, and fired at 840 °C for 30 min. Their dielectric characteristics and piezoelectric coefficients d_{33} were measured by the LCR meter and quasi-static piezoelectric meter. The ceramics were also ground and polished down to a thickness of about 0.2 mm and coated with gold electrodes to record the room-temperature ferroelectric hysteresis loops by a Radiant Precision Workstation.

Results and discussion The required composition and sintering temperature ranges of the SNN pure phase are determined. For Na^+ contents (x) of 0.56–0.68, SN–NN can be solidly dissolved to obtain a pure phase at high temperatures (*i.e.*, > 1280 °C). As $x = 0.71$ and 0.80, SN–NN can be solidly dissolved at 1200–1360 °C. At the Na^+ content of 0.88, the SN–NN solid solution can be obtained, but it decomposes at higher temperatures (> 1320 °C), accompanying the formation of the secondary NN phase. As the Na^+ content further increases, it cannot be solidly dissolved at 1200–1360 °C.

The maximum density is obtained for SNN ceramics sintered at 1340 °C, and the change in Na^+ content has little effect on the microstructure. The T_c of SNN ceramics increases from 272 °C as $x = 0.56$ to 323 °C as $x = 0.88$ because the crystal structure changes from “unfilled” to “filled” as the Na^+ content increases, thus affecting the degree of crystal distortion. T_c gradually decreases because a minor amount of NN appears at x of 0.88. The dielectric constant (ϵ_r) of SNN ceramics initially increases and then decreases, exhibiting a maximum of 1664 as $x = 0.80$. The dielectric loss ($\tan\delta$) remains at a low value at this point. The remnant polarization P_r (11.49 $\mu\text{C}/\text{cm}^2$) and coercive field E_c (20.99 kV/cm) are both nearly maximized as $x = 0.80$ for SNN ceramics due to the “filled” TTB structure, and the maximum d_{33} value of 34 pC/N is obtained for SNN ceramics as $x = 0.80$, which is consistent with the optimal composition for ferroelectric properties.

Conclusions Based on the XRD patterns, the ceramics with a stable, pure TTB phase could be obtained by sintering at 1200–1360 °C when $x = 0.71$ –0.80, and the existence of this phase depended on the ceramic composition and the sintering temperature. As the Na^+ content increased, T_c initially increased because the filling degree of the TTB structure increased, and then gradually decreased when $x > 0.88$ because the increase in Na^+ content induced the formation of the secondary NN phase. When $x = 0.71$ –0.88, the electrical properties could be optimal. The ceramic with x of 0.80 demonstrated a high ferroelectric performance (*i.e.*, $P_r = 11.49 \mu\text{C}/\text{cm}^2$, and $E_c = 20.99 \text{ kV}/\text{cm}$). This study could provide certain theoretical basis and technical support for the subsequent studies of SNN ceramics.

Keywords strontium niobate-sodium niobate binary solid solution; ceramic concentration; sintering temperature; ferroelectric performance