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Sintering and Dielectric Properties of Perovskite SrTaO₂N Ceramics

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Single-phase perovskite oxynitride SrTaO₂N ceramics were prepared by pressureless sintering at 1400 °C under a nitrogen atmosphere, using 5 wt% of SrCO₃ or La₂O₃ as a sintering additive. In contrast, SrTaO₂N bulks without additives contained TaC and Ta₃N₅ impurities. Sintering in nitrogen led to oxygen/nitrogen deficiencies in the oxynitride, while post annealing in flowing ammonia was effective to eliminate the anion vacancies. The introduction of additives significantly improved the sinterability of SrTaO₂N ceramics. A relative density of >90% in the bulk was achieved with a highly dense microstructure with smaller grain sizes. The SrTaO₂N bulk with SrCO₃ additive exhibited superior dielectric performance with a high relative permittivity ($\epsilon_r = 1.0 \times 10^4$) and dissipation factor ($\tan \delta = 0.039$) at a frequency of 1 MHz.

Keywords: Perovskite oxynitrides; Sintering; Dielectric property; Sintering additives

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Introduction

High-permittivity dielectric materials play a significant role in microelectronics, due to their numerous technological applications such as capacitors and memory devices. To date, the most widely used dielectric ceramics are lead-based perovskite ferroelectrics or relaxor oxides, *e.g.*, $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) [1,2]. However, the toxicity of lead and its high vapor pressure during sintering have led to a demand for alternative environmentally friendly lead-free dielectric materials.

Recently, perovskite transition metal oxynitrides with the general formula of $AB(\text{O,N})_3$ have drawn much attention due to their superior dielectric properties [3-7]. Within the oxynitride family, samples of the SrTaO_2N ceramic were reported to possess large dielectric permittivity of ca. 2900 with moderate temperature dependence over the range of 180-300 K [3]. To date, the origin for this dielectric behavior has been studied on the basis of structural investigations [3,8,9]. It is suggested that the *cis* arrangement of nitrogen in TaO_4N_2 octahedra may induce tilting of each octahedron [9]. In SrTaO_2N with statistically-averaged centrosymmetric $I4/mcm$ space group, the coupling of anion ordering with octahedral tilting could lead to structural arrangements that possess a local dipole, which displays a similarity to the polar nanoregions (PNRs) in relaxor ferroelectrics [10]. Accordingly, the nonzero polar momentum units in SrTaO_2N result in high dielectric permittivity under an applied electric field. SrTaO_2N ceramics with large permittivity are stable in air, water and even in

concentrated acids.

One of the problems pertaining to dielectric oxynitride ceramics is the difficulty in fabricating high-density ceramics. There are only a few reports on dielectric oxynitrides [3-7], especially in the ceramic form [3]. The reported SrTaO_2N bulks have considerable porosity (~45%) when sintered by means of a conventional method, which is far from ideal for assessment of the inherent dielectric properties, because these measurements are always affected by the grain interfaces. Therefore, the densification of SrTaO_2N ceramics is necessary for fundamental characterization and also for practical applications, and should therefore be subject to further careful investigation. Hot pressing, hot isostatic pressing and spark plasma sintering are often used to achieve the densification of ceramics. However, these techniques are expensive when applied to mass production in commercial applications. Therefore, we have considered pressureless sintering with certain additives as a far more practical solution. The sintering of dielectric perovskite oxides can be promoted by the addition of A-site donor dopants because the densification kinetics is enhanced by the subsequently-induced A-site defects [11-13]. Meanwhile, during the sintering process of dielectric materials, incorporation of suitable additives could compensate the loss of easy-to-volatilize components. Yang *et al.* reported that the evaporation of PbO in PMN could be compensated by doping with SrO , resulting in the decrease of sintering temperature from 1200 to 800 °C as well as smaller grain sizes [14]. In addition, the dielectric properties can also be improved using specific dopants.

For instance, Kim *et al.* reported that the relative dielectric permittivity of La-modified PbTiO_3 with A-site vacancies was an order of magnitude larger than those of relaxor ferroelectrics [15]. Meanwhile, for PZT ceramics the isovalent substitution of Sr^{2+} for Pb^{2+} at the A-site led to a high dielectric constant of $1.0\text{-}1.3 \times 10^3$ due to the increased tetragonality [16]. Accordingly, SrCO_3 and La_2O_3 can be considered as potential sintering additives for the development of dense SrTaO_2N bulks with high permittivity.

In the present work, the pressureless sintering, microstructure, and dielectric performance of SrTaO_2N ceramics with and without additives was investigated. To the best of our knowledge, this is the first report on the sintering behavior of SrTaO_2N with resulting high relative density.

Experimental Procedure

The perovskite oxynitride SrTaO_2N was synthesized by ammonolysis of precursors obtained from a citrate route [17]. Stoichiometric amounts of SrCO_3 (Wako Pure Chemicals, 99.9%) and TaCl_5 (Sigma-Aldrich, 99.99%) powders were dissolved in 60 mL of anhydrous ethanol, in which citric acid (Wako Pure Chemicals, 98.0%) was added as a complexing agent. The amount of citric acid was equimolar to that of the Ta ions. The solution was heated and stirred at 150 °C to promote polymerization. The resultant viscous gel was then pre-fired at 350 °C for 1 h, which resulted in brownish amorphous oxide precursors. The ammonolysis

reaction was carried out in flowing ammonia (Sumitomo Seika Chemicals, 99.9%, 50 mL/min) at 1000 °C with a heating rate of 5 °C/min, then held for 12 h before cooling to room temperature.

The as-nitrided SrTaO₂N powders were mixed with 5 wt% SrCO₃ or La₂O₃ (Sigma-Aldrich, 99.9%; fired at 970°C for 4 h prior to use) as an additive. Our preliminary experiments indicated that the sintered density and dielectric permittivity of SrTaO₂N ceramics increased significantly when the additive amount was 5 wt% but further excessive addition had negative effects. These powders were die-pressed into 7 mm diameter and 2 mm thick disks, followed by cold isostatic pressing (CIP) at 150 MPa. SrTaO₂N and SrTaO₂N with SrCO₃ or La₂O₃ additive (hereafter denoted as SrTaO₂N-Sr and SrTaO₂N-La, respectively) were placed in a BN crucible and sintered at 1400 °C for 3 h under a nitrogen pressure of 0.2 MPa using a graphite furnace (High Multi 500; Fuji Dempa Kogyo). The sintered bulks were then annealed at 1000 °C for 12 h in flowing ammonia. This post-annealing procedure was necessary to obtain highly resistive bulks for reliable dielectric property measurements.

The SrTaO₂N products were characterized using X-ray diffraction (XRD) with Cu K α radiation (Rigaku, Ultima IV). The data were collected over the angular range of 10-120° with a step size of 0.02°. A counting time of 2.0 s per step was used for the phase identification, while a longer counting time of 9.0 s per step was required for the structural refinement. The

lattice parameters of the SrTaO₂N products, including as-nitrided powder, as-sintered and post-annealed bulks (in powder form), were refined by the Rietveld method using RIETAN2000 software [18]. The bulk density was measured by both the geometric and Archimedes methods. Scanning electron microscopy (SEM; Jeol JSM-6390LA) was used to observe the microstructure of the ceramics. The post-annealed samples were polished with a 4000-grit sandpaper (particle size: 3 μm) to obtain parallel surfaces and then coated with silver paste to act as electrodes. The dielectric properties were measured with impedance analyzers (Yokogawa-Hewlett-Packard, 4274A; Hewlett-Packard, 4285A) in the frequency range from 10² to 10⁶ Hz at room temperature. The impedance plots were fitted and extrapolated using the Cole-Cole empirical relation [19].

Results and discussion

Figure 1 shows XRD patterns for the SrTaO₂N powder, as-sintered SrTaO₂N and post-annealed SrTaO₂N bulks with and without sintering additives. Compared with the as-nitrided powder, a small amount of TaC impurity was detected in the as-sintered SrTaO₂N bulk without any additive. The TaC impurity is likely to form when excess Ta is combined with organic residue due to the loss of SrO from SrTaO₂N during sintering. To minimize the amount of organic residue in the precursor powder, the combustion at 600 °C was examined, but this procedure did not lead to a reduced amount of TaC in the as-sintered SrTaO₂N bulk.

In spite of the high melting temperature, SrO loss may occur in high-temperature processing, as reported in SrTiO₃, SrZrO₃ and Sr₂RuO₄ [20-22]. The diffraction peaks of TaC impurity disappeared in the as-sintered SrTaO₂N-Sr and SrTaO₂N-La bulks because Sr²⁺ or La³⁺ from the additives compensates the Sr loss, which inhibits the appearance of this secondary phase. It was found that all the sintered bulks changed from brown to dark gray, which indicates reduction of the tantalum associated with anion deficiencies in the crystal lattice. Post-annealing in an ammonia atmosphere was necessary because heat treatment in air/oxygen leads to oxidation and decomposition of the oxynitrides [23]. After the annealing process, TaC and Ta₃N₅ impurities were observed in SrTaO₂N without additives, while both SrTaO₂N-Sr/La samples were phase-pure perovskites. At high temperatures, the TaC impurity was oxidized and then nitrided in ammonia to form Ta₃N₅ in the post-annealed SrTaO₂N bulk [24], as indicated in Fig. 1(e). We tentatively believe that a trace amount of oxygen from the not-fully airtight furnace is the oxidizing agent. It can be assumed that a part of TaC was not oxidized and still remained as it was, due to the limited amount of oxygen.

The XRD patterns were refined to obtain the lattice parameters of the SrTaO₂N products, including the as-nitrided powder, as-sintered and post-annealed bulks, based on the tetragonal *I4/mcm* space group [9]. A summary of the crystallographic features is given in Table 1. Rietveld refinement plots for the SrTaO₂N products are given in the Supporting Information. A trace amount (0.43 wt%) of SrCl₂·2H₂O impurity was observed in the as-nitrided powder.

The c parameter of the tetragonal lattice was slightly reduced in the as-sintered bulk. Recovery of the c value was then achieved by annealing in ammonia, which was accompanied by the color change from dark gray to brown. The lattice parameter variations upon sintering/post-annealing were reproducible in different sample batches. It is thus reasonable to interpret the lattice parameter variations as a hint for the changing anion vacancy contents upon sintering/post-annealing. Anion vacancies are assumed to be introduced during the high temperature sintering, because the thermal reduction environment in the graphite dies led to oxygen/nitrogen deficiency. However, the anion vacancies should be mainly ascribed to a loss of nitrogen because the reported standard free energy of formation is much lower for metal nitrides than for the corresponding oxides [25]. Compared with transition metal oxides, the relatively low stability of the associated nitrides, related to weaker bonding, has already been understood through theoretical calculations [26]. Therefore, the loss of nitrogen is more likely to occur by heating SrTaO_2N at 1400 °C, which results in shrinking of the crystal lattice due to its covalent nature. The formation of nitrogen vacancies may involve the release of N_2 gas, as suggested by the previous thermogravimetric study [23]. Similar results have been documented in nonstoichiometric metal nitrides, such as TiN_x and $\delta\text{-NbN}_x$ [27].

The relative densities of the post-annealed SrTaO_2N , $\text{SrTaO}_2\text{N-Sr}$ and $\text{SrTaO}_2\text{N-La}$ bulks were 70, 93, and 90%, respectively. The SrTaO_2N bulk without additives could not be well sintered, while a high density was achieved at 1400 °C by the addition of 5 wt% SrCO_3 or

La₂O₃. The fracture surface morphology did not change with the post-annealing, but was changed by the addition of sintering additives, as shown by the SEM micrographs in Fig. 2. After the annealing process, densification and smaller grain size was achieved with the sintering additives. The SrTaO₂N bulk without additives was porous with large voids between the grains, indicating insufficient densification. In contrast, the SrTaO₂N ceramics sintered with additives were considerably dense and consisted of a well-developed microstructure. The reason lies in that the SrO (from SrCO₃) or La₂O₃ could react with Sr-deficient SrTaO₂N (Sr_{1-δ}TaO₂N) to promote the efficient reaction sintering and further densification, while no obviously segregated compounds such as strontium tantalum oxides and lanthanum tantalum oxides were observed in the microstructures. Take the SrTaO₂N-La as an example, La³⁺ could partly substitute the A-site Sr²⁺, due to their similar ionic radii [28]. The entropy gain by (Sr_{1-x}La_x)Ta(O,N)_{3-δ} solid solution formation are beneficial to mass transport and enhancement of the densification process. The loss of SrO offered an opportunity for the reaction sintering after the incorporation of additives, which was found to be necessary to obtain relatively dense SrTaO₂N bulks. It is noteworthy that smaller grains were obtained in the SrTaO₂N-Sr/La ceramics. As the densification occurs, Sr²⁺/La³⁺ appears not only in the bulk regions but also near grain boundaries due to the relatively high additive level, resulting in the inhibition of grain growth as well as the smaller grain sizes [29-31].

All the as-sintered SrTaO₂N ceramics exhibited semiconductive behavior, typically with

several thousand ohms at room temperature. The successive heat treatment in ammonia was found to be essential to recover the dielectric properties which accompany resistance values several order of magnitudes larger than those of the as-sintered bulks. Figure 3 shows the dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) as a function of frequency for the post-annealed SrTaO₂N samples. Both the ϵ_r and $\tan \delta$ values decrease with increasing frequency. The SrTaO₂N bulk samples without additives have ϵ_r values in the order of 1.8×10^3 at 10^2 Hz, which is lower than that reported previously [3], despite its relatively higher density. It seems that the presence of secondary phases such as TaC and Ta₃N₅ is responsible for the lower dielectric constant. In contrast, the addition of SrCO₃ or La₂O₃ resulted in a significant increase in the dielectric constant, which was enhanced to 1.6×10^4 . This value is several times higher than the permittivity (~ 2900) reported by Kim *et al.* [3]. The permittivity of SrTaO₂N-Sr/La ceramics is comparable to those reported for ferroelectric and relaxor oxides at their Curie temperatures [32]. Another intriguing feature of SrTaO₂N with additives is the weak dependence of the dielectric constant on frequency, *e.g.*, SrTaO₂N-Sr had high relative permittivities of 1.7×10^4 , 1.3×10^4 , and 1.0×10^4 at frequencies of 10^2 , 10^4 , and 10^6 Hz, respectively. The dielectric constants of the SrTaO₂N ceramics are sensitive to density. Enhanced densification is beneficial to obtain desirable dielectric properties. Accordingly, the highly densified SrTaO₂N-Sr/La bulks with uniform grain structure also exhibit much higher room-temperature dielectric constants than SrTaO₂N without additives.

It is worthy to note that the dielectric loss for the present SrTaO₂N bulk without additives is comparable to that obtained for a LaTiO_xN_y thin film [5], which is an order of magnitude lower than that reported for the SrTaO₂N bulk in the previous work [3]. It has been indicated that the dielectric loss decreases significantly as the sample sintering improves, while the electrical conductivity remains low [3]. The present SrTaO₂N-Sr/La bulks has a significantly improved grain microstructure, but the dielectric loss is relatively high. The $\tan \delta$ values are all approximately 0.04 at 1 MHz, which is still higher than that required for practical applications. The number of grain boundaries was increased in the SrTaO₂N-Sr/La bulks due to the smaller grain size, leading to an accumulation of the space charge [33]. This may be one reason for the high dissipation factor. In addition, the formation of lattice defects within the crystal also affects the dielectric loss. The SrTaO₂N ceramics with additives are well densified; therefore, it is likely that the anion deficiencies were not completely removed during the post annealing process. A small amount of anion vacancies (or tetravalent tantalum) is sufficient to cause a large increase in the dielectric loss [34]. Such Ta⁴⁺ species with paramagnetic moments should be detectable by means of electron paramagnetic resonance and be subject to further exploration. A similar result was also reported for BaTi₄O₉/Ba₂Ti₉O₂₀-based ceramics, where even a low defect density caused by reductive heat treatment significantly increased the dielectric loss [35].

Complex impedance plots of the SrTaO₂N and SrTaO₂N-Sr/La bulks are shown in Fig. 4.

To interpret these impedance spectra, an equivalent circuit model consisting of two parallel RC elements connected in series was assumed. These two serial RC units represent the bulk (R_b) and grain boundary (R_{gb}) contributions [3]. For the SrTaO₂N-Sr/La bulks, the first semicircle corresponding to the bulk contribution was clearly observed, whereas the low frequency ($<10^2$ Hz) semicircle related to the grain boundaries was not evident due to the instrumental limitations of the experimental range. It has been recognized that the choice of the electrical contact type sometimes influences the overall electrical behaviors [36]. Nevertheless, effects of the electrodes are assumed to be insignificant, since different contact types (here Ag-pasted and Pt-sputtered electrodes) resulted in essentially similar results, as presented in Supporting Information. The R_b value, assigned as the intercept of the Z' -axis in the Cole-Cole plot, is quite different among the SrTaO₂N and SrTaO₂N-Sr/La bulks. The impedance spectrum of the SrTaO₂N bulk without additives did not form a semicircle, which is indicative of a much higher value for R_b . The lower bulk resistance of the SrTaO₂N-Sr/La bulks can be attributed to the presence of residual oxygen/nitrogen deficiencies. However, for the SrTaO₂N bulk without additives, the anion vacancies are easily removed from the porous ceramic body to reach cation-anion stoichiometry. Accordingly, a more resistive bulk gave rise to a large semicircle in the impedance spectrum. For dielectric materials, low values of electrical resistance often lead to high dielectric loss; the increase in $\tan \delta$ with the SrCO₃ or La₂O₃ additives could be related to the smaller bulk resistance.

In the present work, the dielectric permittivity of the dense SrTaO₂N ceramics is extremely high and comparable with the giant ϵ_r reported for the rocksalt-type Li, Ti co-doped NiO [37]. In addition, the thermal stability of SrTaO₂N can be ensured up to 480 °C in air [23], which is much higher than the Curie temperature of PZT [1], where a huge variation of permittivity occurs. Although the method of densification has been developed for the dielectric SrTaO₂N ceramics, the dielectric loss should be further reduced by eliminating anion vacancies in a considerably improved microstructure.

Conclusion

Pressureless sintering was applied to fabricate dielectric oxynitride SrTaO₂N ceramics using sintering additives. Both SrCO₃ and La₂O₃ were effective to achieve single-phase SrTaO₂N bulks with relative densities higher than 90%. The incorporation of sintering additives in the SrTaO₂N ceramic led to a well-developed microstructure with smaller grain sizes. The residual porosity of SrTaO₂N ceramics was necessary to remove anion vacancies during the post-annealing treatment in ammonia to realize smaller dielectric losses. The room temperature ϵ_r values of SrTaO₂N-Sr and SrTaO₂N-La were 1.7×10^4 and 1.6×10^4 at 100 Hz, respectively; however, in contrast, the SrTaO₂N without additives exhibited lower dielectric permittivity of approximately 1.8×10^3 due to the much higher porosity, the presence of secondary phases as well as the possible grain boundary effects.

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Figure Captions:

Fig. 1. XRD patterns of (a) as-nitrided SrTaO_2N powder, (b) as-sintered SrTaO_2N bulk, (c) as-sintered $\text{SrTaO}_2\text{N-Sr}$ bulk, (d) as sintered $\text{SrTaO}_2\text{N-La}$ bulk, (e) post-annealed SrTaO_2N bulk, (f) post-annealed $\text{SrTaO}_2\text{N-Sr}$ bulk, and (g) post-annealed $\text{SrTaO}_2\text{N-La}$ bulk.

Fig. 2. Scanning electron micrographs of the fracture surfaces of post-annealed (a) SrTaO_2N without additives, (b) $\text{SrTaO}_2\text{N-Sr}$, and (c) $\text{SrTaO}_2\text{N-La}$ bulks.

Fig. 3. Relative dielectric constants (ϵ_r) and dielectric losses ($\tan \delta$) of post-annealed (a) SrTaO_2N without additives, (b) $\text{SrTaO}_2\text{N-Sr}$, and (c) $\text{SrTaO}_2\text{N-La}$ bulks as a function of frequency.

Fig. 4. Impedance spectra for the post-annealed SrTaO_2N ceramics measured at 10^2 - 10^6 Hz.

Table 1.

Summary of structural refinement details for the as-nitrided SrTaO₂N powder, as-sintered and post-annealed SrTaO₂N products.

	As-nitrided	As-sintered	Post-annealed
Crystal system	Tetragonal		
Space group	<i>I4/mcm</i>		
<i>a</i> (nm)	0.5700(3)	0.5701(3)	0.5701(5)
<i>c</i> (nm)	0.8078(2)	0.8068(4)	0.8076(4)
<i>c</i> / $\sqrt{2}a$	1.0021	1.0006	1.0017
Volume (10 ⁻²⁷ m ³)	0.2625(4)	0.2622(2)	0.2625(3)
ρ_{calc} (Mg·m ⁻³)	7.9607(3)	7.9680(5)	7.9613(2)
SrTaO ₂ N (wt%)	99.57	97.68	98.13
TaC (wt%)	--	2.32	0.89
Ta ₃ N ₅ (wt%)	--	--	0.98
<i>R</i> _{wp} (%)	7.13	9.32	9.37
<i>S</i>	1.94	2.48	2.49

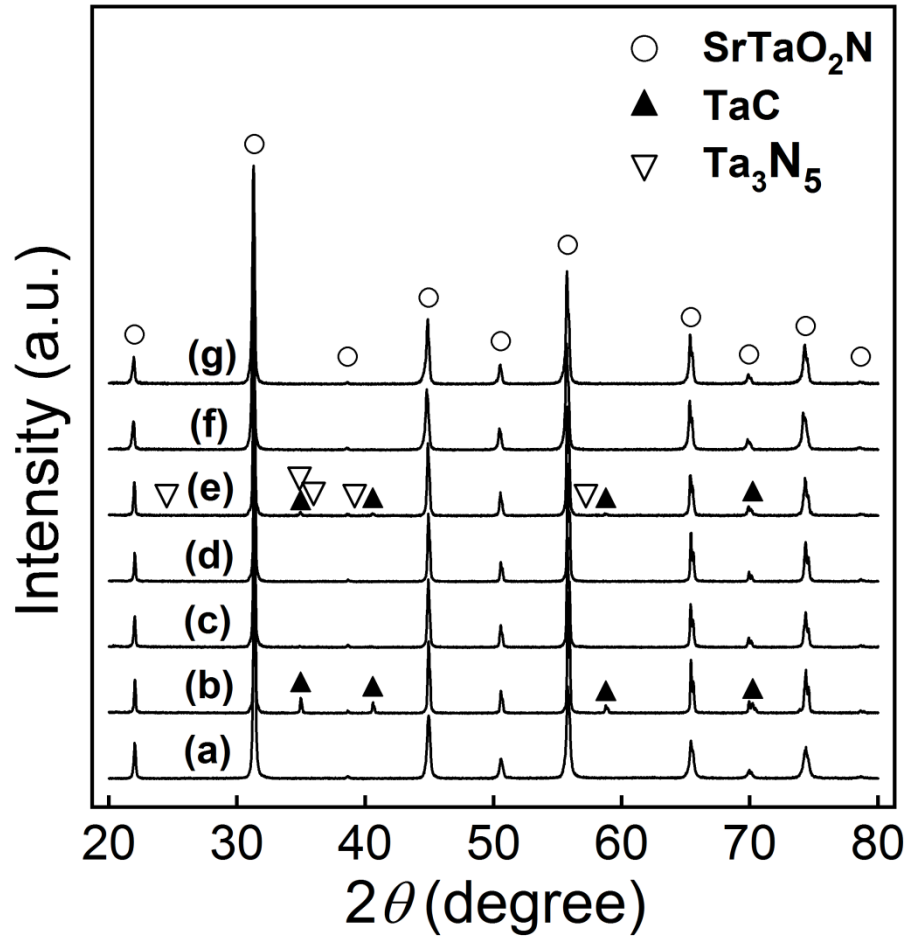


Fig. 1. XRD patterns for (a) as-nitrided SrTaO_2N powder, (b) as-sintered SrTaO_2N bulk, (c) as-sintered SrTaO_2N -Sr bulk, (d) as sintered SrTaO_2N -La bulk, (e) post-annealed SrTaO_2N bulk, (f) post-annealed SrTaO_2N -Sr bulk, and (g) post-annealed SrTaO_2N -La bulk.

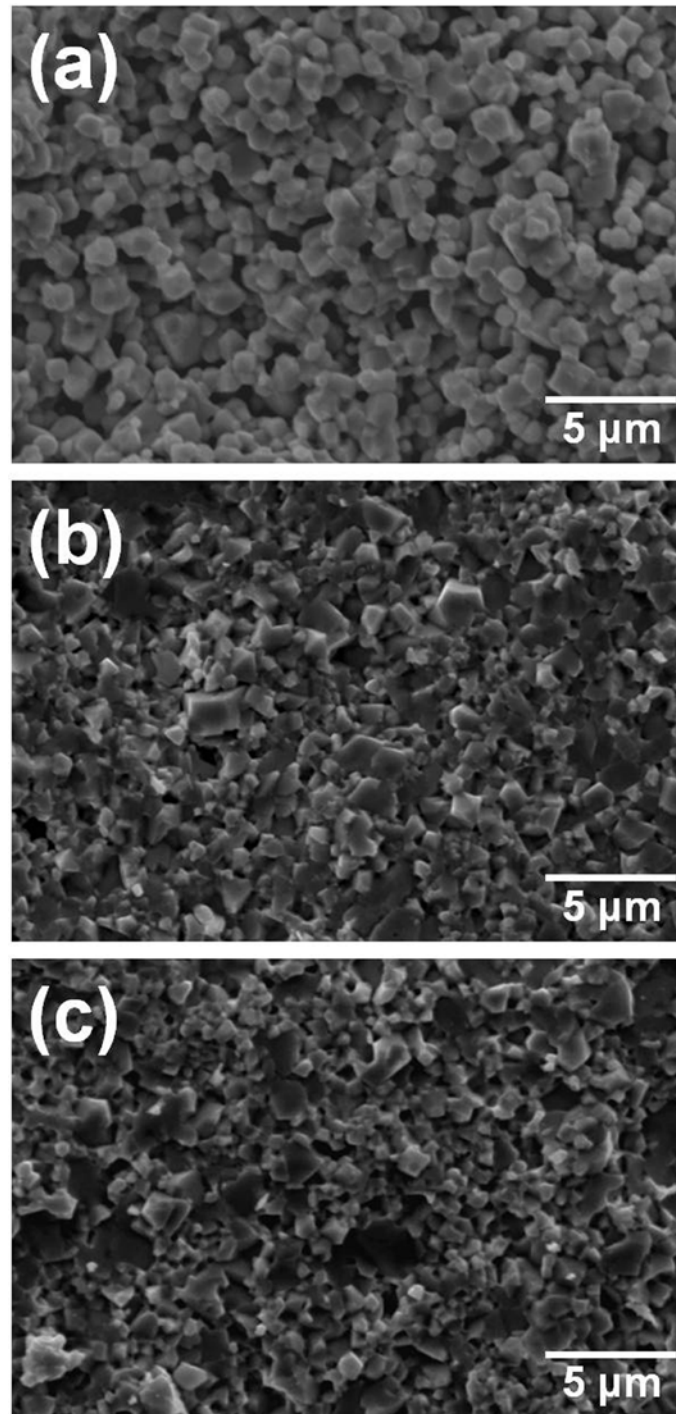


Fig. 2. Scanning electron micrographs of the fracture surfaces of post-annealed (a) SrTaO_2N without additives, (b) $\text{SrTaO}_2\text{N-Sr}$, and (c) $\text{SrTaO}_2\text{N-La}$ bulks.

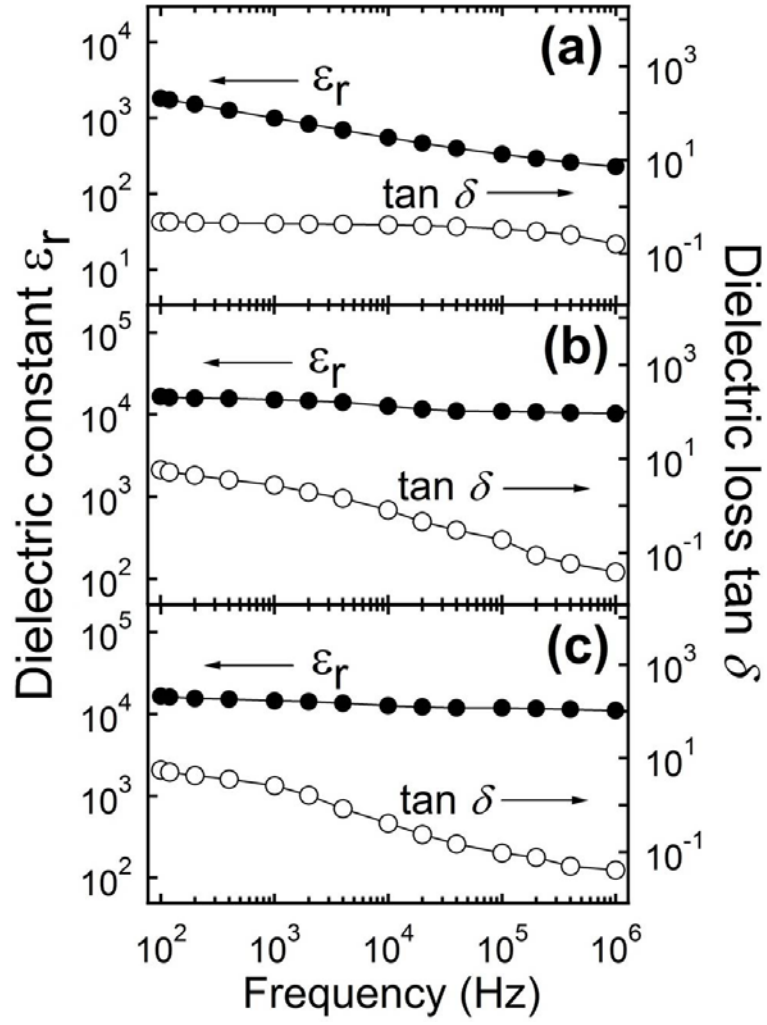


Fig. 3. Relative dielectric constants (ϵ_r) and dielectric losses ($\tan \delta$) of post-annealed (a) SrTaO_2N without additives, (b) $\text{SrTaO}_2\text{N-Sr}$, and (c) $\text{SrTaO}_2\text{N-La}$ bulks as a function of frequency.

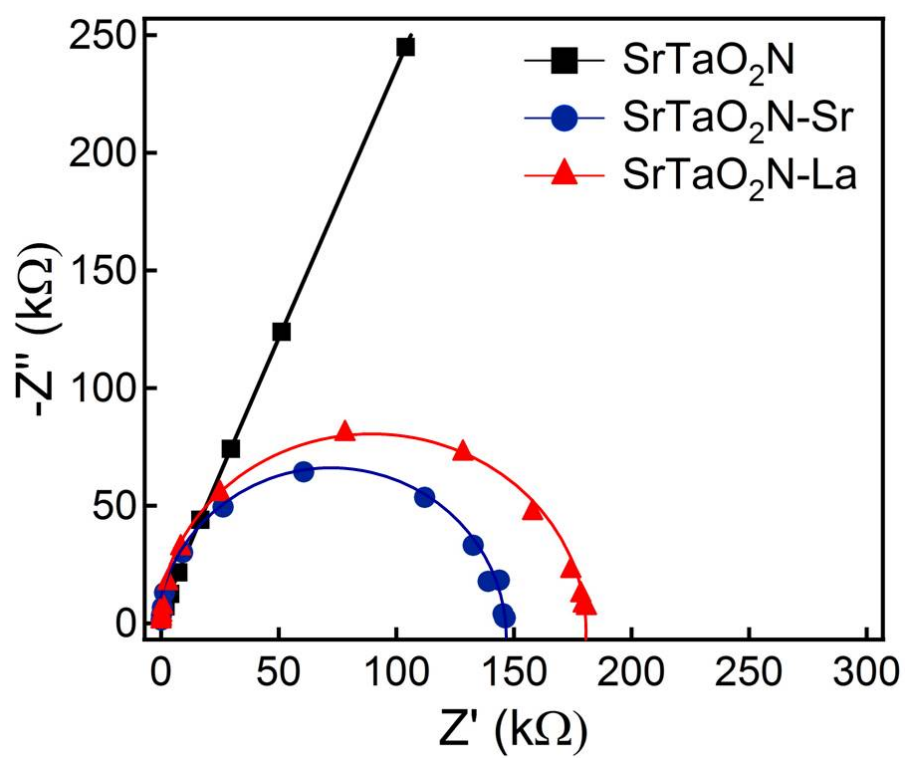


Fig. 4. Impedance spectra for the post-annealed SrTaO₂N ceramics measured at 10^2 - 10^6 Hz.