

Effect of sintering additives on the densification and dielectric properties of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ ceramics synthesized by a soft-chemistry method

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Abstract. Nano-crystalline $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ powders with addition of LiNbO_3 or LiF as sintering additives were prepared by a soft-chemistry synthesis using polyethylene glycol. Calcination at 600 °C results in nanocrystalline powders ($d_{\text{cryst.}} \approx 30$ nm) which were sintered between 1000 and 1300 °C to ceramic bodies. By addition of 10 and 20 mol% LiNbO_3 , the sintering temperature was reduced by about 200 K and the activation energy of the initial stage of sintering decreases from 386 to 271 kJ mol^{-1} . The sintering aid improves the grain growth and dense ceramic bodies were obtained after sintering at 1125 °C for 1 h. A higher LiNbO_3 content favors the formation of a pillar-like microstructure. XRD patterns of ceramics sintered above 1000 °C show only reflections of the $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ phase indicating an incorporation of LiNbO_3 in the $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ structure. Dielectric measurements reveal a diffuse phase transition and a relaxor-like behavior. The phase transition temperature (T_m) depends on the sintering conditions and is between 117 and 127 °C for 10 mol% LiNbO_3 , which is very close to pure $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$, while addition of 20 mol% shifts T_m to around

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200 °C and the transition becomes slightly more diffuse. The optical band gap of the samples is ≈ 3.3 eV and depends slightly on the sintering conditions. We also tried LiF as sintering aid, but this leads to the formation of considerable amounts of secondary phases in the ceramics and relative densities of only 82 %.

Keywords: sintering aid, permittivity, strontium barium niobate, band gap, lithium niobate, relaxor

1. Introduction

As a lead-free and eco-friendly alternative to e.g. PZT (lead zirconate titanate), strontium barium niobate, $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBN), is an interesting candidate because of its ferroelectric, pyroelectric, piezoelectric, electro-optic, and photorefractive properties [1–4]. Due to its ferroelectric behavior, SBN is also used in magnetoelectric composites [5–7]. Furthermore, some authors report about photocatalytic activities [8,9]. $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ is ferroelectric in the x range from 0.25 to 0.75 and crystallized in the tetragonal tungsten-bronze (TTB) structure. Its ferroelectric properties are sensitive to the composition and preparation procedure [10,11]. With rising strontium content an increasing relaxor behavior can be observed [12]. For $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$, the permittivity maximum (T_m), which reflects the ferroelectric $\rightleftharpoons$ paraelectric phase transition, is between 110–130 °C for single crystals [3,11], while for polycrystalline samples values between 40 and 177 °C have been reported [13–17].

Usually, $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ is synthesized by the conventional mixed-oxide method which leads to coarse-grained powders. Additionally, few soft-chemistry syntheses have been reported to produce sub-micro or nano-sized powders [14,18–21]. Compacts of strontium barium niobate reveal moderate densification behaviour. Thus, sintering to dense ceramic bodies requires

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high temperatures and long soaking times [14–22]. The densification behavior and the grain growth can generally be improved using sintering additives [23,24]. For example, Wang et al. [25] used SiO_2 as additive to decrease the sintering temperature. Due to the addition of SiO_2 , T_m is shifted to lower temperatures. On the other hand, some authors utilized V_2O_5 as additive (liquid phase sintering) and observed an increase of T_m [26–28]. Furthermore, addition of Bi_2O_3 , PbO and Nb_2O_5 enhance the densification and influence the dielectric behavior marginally [27].

In this work, we investigated the influence of LiNbO_3 and LiF on the sintering and dielectric behavior of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$. The samples were synthesized by a one-pot soft-chemistry method leading to nano-scaled preceramic powders. Phase evolution and microstructure of ceramics bodies were monitored by XRD and SEM. The sintering behavior was investigated up to 1350 °C. Additionally, the samples were characterized by diffuse reflectance and dielectric measurements.

2. Experimental

2.1. Material preparation

All samples were synthesized according to the one-pot soft-chemistry method as described earlier [14]. The amount of the added sintering additive is related to the amount of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$. For the addition of LiNbO_3 , the initial compositions of the samples were as follows: 1 mol $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6 + x$ mol LiNbO_3 with $x = 0.1$ and 0.2 ($= 3.75$ and 7.50 wt%), abbreviated as $\text{SBN}+\text{LN}-x$.

In a typical reaction, 0.02 mol NbCl_5 (Alfa Aesar, 99 %) was dissolved in 25 ml 2-methoxyethanol. 50 ml polyethylene glycol (PEG400) and 52 g citric acid were added under stirring on a heating plate at 150 °C until a clear solution resulted. Equimolar amounts of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck, ≥ 99 %) and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (Fluka, ≥ 99 %) were solved together in 10 ml

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1,2-ethanediol and $\text{Li}(\text{CH}_3\text{COO})\cdot 2\text{H}_2\text{O}$ (Chemapol, purum) was solved in 5 ml 1,2-ethanediol. The amounts of the Sr-, Ba-, and Li-compounds are calculated as $n_{\text{Sr}} = n_{\text{Ba}} = n_{\text{Nb}}/(2[2+x])$ and $n_{\text{Li}} = n_{\text{Nb}}\cdot x/(2+x)$ ($x = 0.1$ and 0.2 ; molar fraction of LiNbO_3 related to the amount of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$). Afterwards, both the (Sr,Ba)- and Li-solutions were added to the hot Nb-solution. The reaction mixture was continuously stirred on the heating plate at $250\text{ }^\circ\text{C}$ for about 3–4 h until it turned to a white highly viscous solution. The resulting (Sr,Ba,Nb,Li)-solutions were calcined at $600\text{ }^\circ\text{C}$ for 2 h (rate 10 K min^{-1}) in static air leading to white nanoscaled powders. Ceramic bodies were fabricated from these powders by mixing with 10 wt% of a saturated aqueous polyvinyl alcohol (PVA) solution as pressing aid and uniaxially pressed at about 71 MPa into pellets (green density: 2.2 g cm^{-3}). These pellets were sintered on a ZrO_2 fibre mat between 1000 and $1300\text{ }^\circ\text{C}$ (heating-/cooling rate 5 K min^{-1}) with a soaking time of 1 h to the final ceramic bodies. These had a thickness of about 1–1.6 mm and diameters of 4–6 mm.

For comparative purposes, pure $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ (abbreviated as SBN) was also prepared according to the aforementioned synthesis.

The common sintering additive LiF was also tested. For this purpose, $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$, prepared as mentioned above, was calcined at $1100\text{ }^\circ\text{C}$ for 2 h (rate 10 K min^{-1}) and mixed in a planetary mill with 76 mol% LiF (= 5.0 wt%, Sigma-Aldrich, 98 %) in a polyamide jar using propane-2-ol and ZrO_2 -balls. After drying, the white powder was pressed and sintered to ceramics as described above. The samples were abbreviated as SBN+LF

2.2. Characterization

X-ray powder diffraction patterns were recorded at room temperature on a Bruker D8-Advance diffractometer, equipped with a one-dimensional silicon strip detector (LynxEye™)

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using Cu- K_α radiation and a counting time of 1 s per data point. Crystallite sizes and strain parameters were calculated from XRD line broadening (integral peak breadth) using the software suite WinXPOW [29] applying the Scherrer and Wilson equations. Differential thermoanalytic (DSC) investigations in flowing synthetic air (50 ml min^{-1}) were performed with a heating rate of 10 K min^{-1} using a Netzsch STA 449F5 system. Atom absorption spectroscopy measurements were carried out with an Agilent AA 280FS. Scanning electron microscope images were collected with a Phenom ProX SEM in backscattered electron mode (BSE). For impedance investigations, the ceramic bodies with a thickness of 1.2–1.4 mm were sputtered on both sides with 100 nm thick gold electrodes using a Cressington Sputter Coater 108auto. An Impedance Analyzer 4192A (Hewlett Packard) was used for frequency- and temperature dependent impedance measurements.

3. Results and discussion

LiF is used as a common sintering additive for various ceramic materials [30–34], therefore we tested LiF to reduce the sintering temperature of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$. Additions of 76 mol% (= 5 wt%) LiF to $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ leads to an enhanced densification at low sintering temperatures with relative densities of 80(1) and 82(1) % after sintering at 1050 °C and 1150 °C, whereas at 1200 °C a reduction to 77(1) % was observed. XRD investigations (Fig. S1, supporting information) of SBN+LF ceramics sintered at 1050 °C and 1200 °C leads to a mixture of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$, $\text{Li}_4\text{Sr}_{3.06}\text{Nb}_6\text{O}_{20}$ (JCPDS #01-089-7516), Li_2O (JCPDS #01-012-0254), and $\text{Ba}_3\text{Nb}_2\text{O}_8$ (JCPDS #01-072-0192). The fraction of secondary phases was calculated to be 25–30 wt%. For that reason, LiF is not suitable as sintering aid for $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$.

3.1. $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6 + \text{LiNbO}_3$

3.1.1. Synthesis and powder characterization

In the following we used LiNbO_3 as sintering aid. 1 mol $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6 + x$ mol LiNbO_3 ($\text{SBN}+\text{LN}-x$) with $x = 0.1$ and 0.2 were synthesized by a one-pot synthesis. To obtain white nanoscaled powders, the viscous (Sr,Ba,Nb,Li)-solutions were calcined at 600°C for 2 h. The XRD patterns (Fig. 1) show only reflections of tetragonal $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ (JCPDS #01-074-6520) and rhombohedral LiNbO_3 (JCPDS #01-078-0250), however an increasing background level around $2\theta = 30^\circ$ indicates an amorphous fraction in the samples. The specific surface areas (BET method) were determined to be $32(3) \text{ m}^2 \text{ g}^{-1}$ for $x = 0.1$ and $24(2) \text{ m}^2 \text{ g}^{-1}$ for $x = 0.2$, which correspond to equivalent primary particle sizes of $35(3)$ and $47(3) \text{ nm}$. The volume-weighted average crystallite size of the $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ phase for $\text{SBN}+\text{LN}-0.1$ and $\text{SBN}+\text{LN}-0.2$ is $31(3)$ and $29(3) \text{ nm}$, respectively.

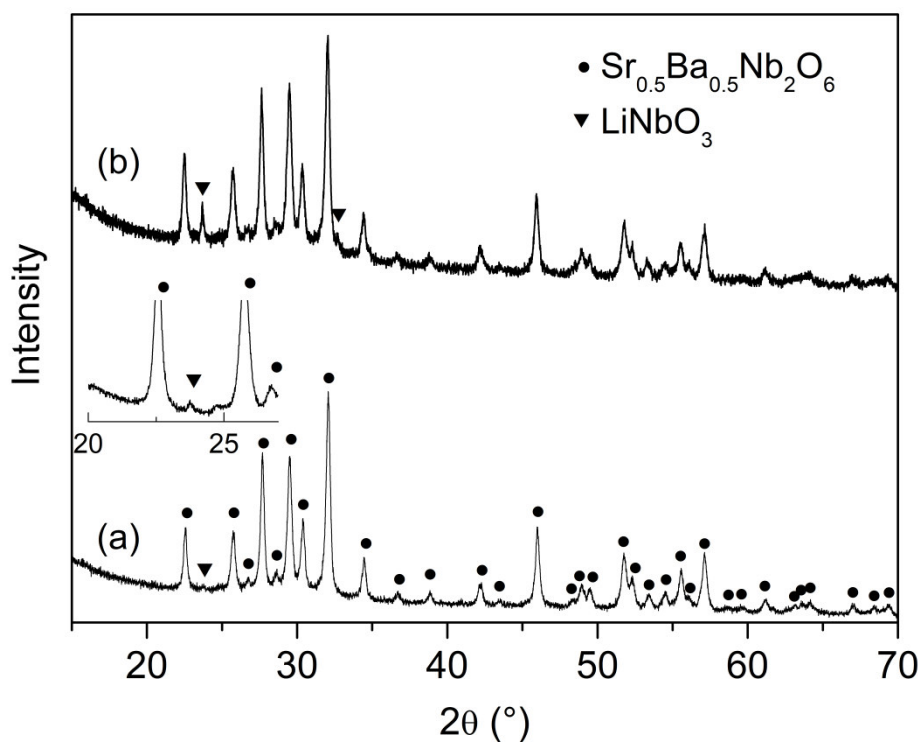


Fig. 1 Room-temperature XRD patterns of $\text{SBN}+\text{LN}-x$ ($= \text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6+x\text{LiNbO}_3$) powders after calcining at 600 °C for 2 h (heating rate 10 K min⁻¹): (a) $x = 0.1$, (b) $x = 0.2$. The insets show a magnification of the XRD pattern for $x = 0.1$ recorded with a prolonged counting time of 10 s per data point.

3.1.2. Sintering, microstructure, and phase composition of the ceramics

Non-isothermal dilatometric measurements of SBN and $\text{SBN}+\text{LN}-x$ ($x = 0.1$ and 0.2) powder compacts up to 1350 °C in flowing air are shown in Fig. 2. The SBN sample starts to shrink slightly at about 1100 °C while at about 1220 °C the shrinkage increases significantly. The shrinking rate achieves a maximum at 1325 °C with $-1.08 \text{ \% min}^{-1}$. The $\text{SBN}+\text{LN}-x$ compacts with the sintering additive show an improved shrinkage behavior. A first slight shrinkage begins around 700 °C, whereas a considerable densification process starts at 1150 °C ($\text{SBN}+\text{LN}-0.1$) and 1000 °C ($\text{SBN}+\text{LN}-0.2$), respectively. The shrinkage maxima are shifted to lower temperatures of 1300 °C and 1209 °C with values in both cases of $-1.28 \text{ \% min}^{-1}$ as shown in the inset of Fig. 2. The shrinkage rates of the three samples points to viscous flow (sliding process of whole grains) as a dominant shrinkage mechanism, because diffusion processes cause typical shrinkage rates between 10^{-4} and $10^{-1} \text{ \% min}^{-1}$ [35–38]. Furthermore, DSC measurements of $\text{SBN}+\text{LN}-0.2$ up to 1350 °C did not show any indication of the formation of a liquid phase (Fig. S2, supporting information) indicating that the densification process is caused by solid-state phase sintering. The activation energy of the initial state of sintering can be calculated from the non-isothermal dilatometric measurements applying the equation for the constant heating rate (CHR) method (1) [39,40].

$$T^2 \left(\frac{d\left(\frac{\Delta L}{L_0}\right)}{dt} \right) = \frac{2aE_a}{nR} \cdot \frac{\Delta L}{L_0} \quad (1)$$

where, T = temperature, $\Delta L L_0^{-1}$ = relative shrinkage, t = time, a = heating rate, n = constant depending on the mechanism of initial stage of sintering, E_a = activation energy, R = universal gas constant. As mentioned above, the initial stage of sintering can be described by the viscous flow mechanism ($n = 2$ [39]). Thus, E_a can be calculated from the slope by plotting the left hand-side of equation (1) versus $\Delta L L_0^{-1}$ (as depicted in Fig. 3) For $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ the activation energy for the initial stage of sintering was calculated as $386(22) \text{ kJ mol}^{-1}$, which is significantly lower than the activation energy of 825 kJ mol^{-1} found for coarse-grained $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ synthesized by the conventional mixed-oxide method [41]. By addition of LiNbO_3 the activation energy decreases to $300(18)$ and $271(15) \text{ kJ mol}^{-1}$ for SBN+LN-0.1 and SBN+LN-0.2, respectively.

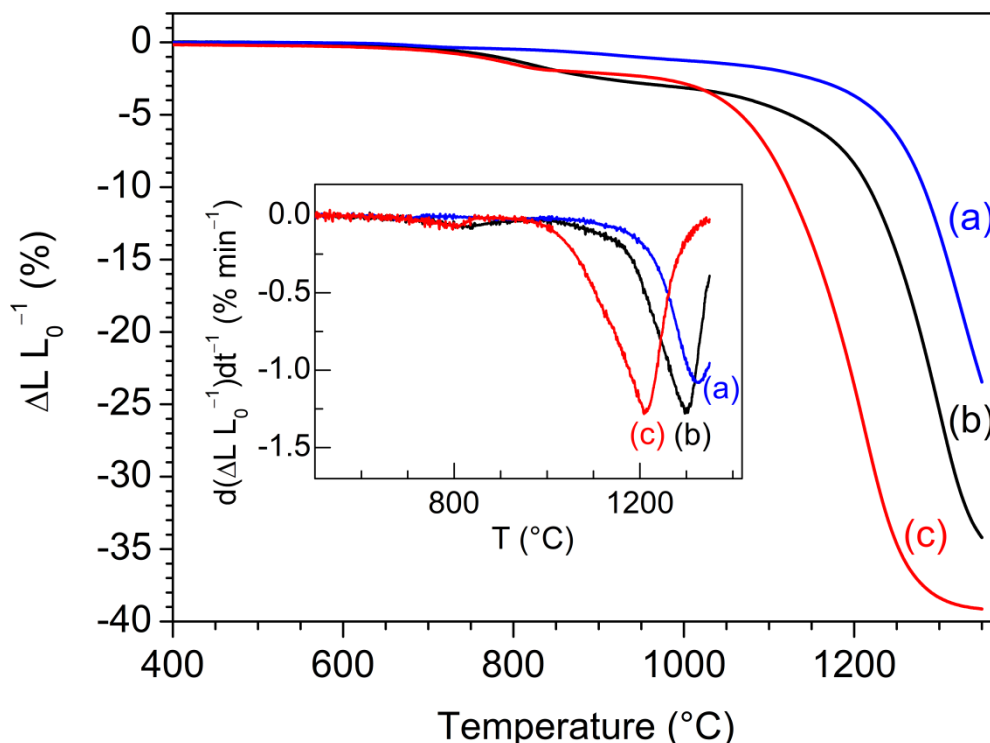


Fig. 2 Non-isothermal dilatometric measurements up to 1350 °C (heating rate 5 K min⁻¹) in flowing air of (a) SBN, (b) SBN+LN-0.1, (c) SBN+LN-0.2 of compacted powders calcined at 600 °C. The inset shows the shrinkage rates.

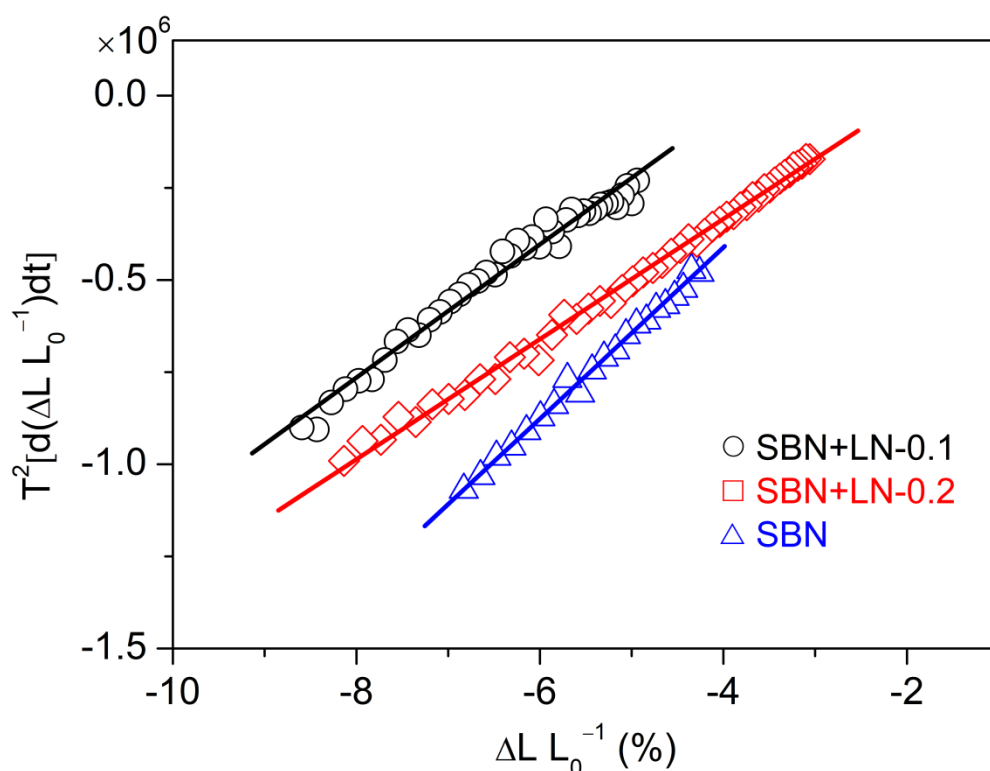


Fig. 3 Plot of $T^2[d(\Delta L/L_0^{-1})/dt]$ vs. $\Delta L/L_0^{-1}$. For the sake of clarity, every 30th data point is marked by a symbol. Solid lines are the fit results.

Based on these results, for further investigations the nanocrystalline powders were pressed to pellets and sintered in static air at temperatures between 1000 and 1300 °C for 1 h (heating-/cooling rate: 5 K min⁻¹). The bulk densities of the white-yellow ceramics bodies were calculated from their weight and geometric dimensions. The obtained densities are related to the single crystal density of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ [42]. Dense ceramics (relative density ≥ 90 %) of

pure $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ can be only obtained after firing above 1300 °C. In contrast, by the addition of LiNbO_3 densities above 90 % can be obtained already at 1175 °C ($x = 0.1$) and 1125 °C ($x = 0.2$) as shown in Fig. 4. Increasing temperatures raise the relative bulk densities further up to 96(1) %. The SBN+LN-0.2 ceramics show a very slight decrease in density after firing at 1300 °C due to a change in the microstructure as described below. In summary, the use of the sintering additive LiNbO_3 results in dense ceramics at significantly lower temperature and shorter sintering time, compared to pure $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$.

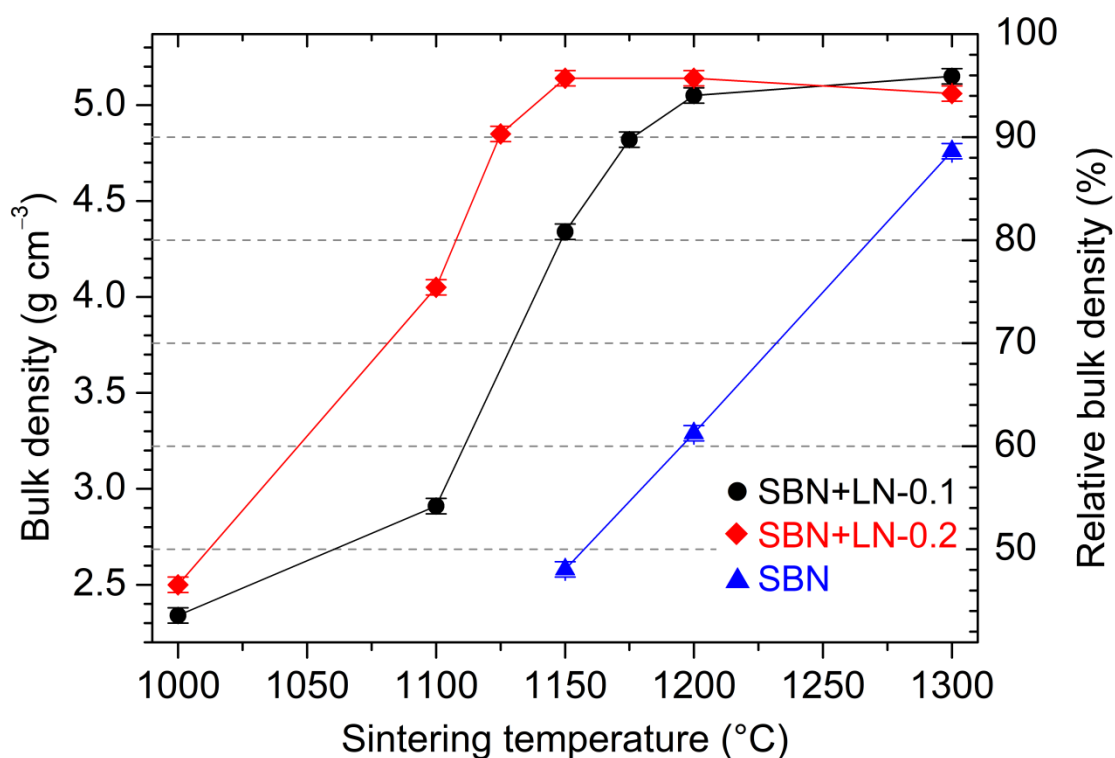


Fig. 4 Bulk densities of ceramic bodies after sintering at various temperatures for 1 h (heating-/cooling rate 5 K min⁻¹).

Typical microstructures of SBN+LN- x ceramics are shown in Fig. 5. The average grain size ($\bar{\phi}_{\text{li}}$) was estimated by counting of at least 700 grains using the lineal intercept method [43]. Ceramics with $x = 0.1$ consist of globular and irregular shaped grains. Their sizes are between

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0.5–3.7 μm ($\bar{\varnothing}_{\text{li}} = 1.7(4) \mu\text{m}$), 1–7 μm ($\bar{\varnothing}_{\text{li}} = 3.0(5) \mu\text{m}$), and 1–18 μm ($\bar{\varnothing}_{\text{li}} = 6(2) \mu\text{m}$) after sintering at 1150, 1200, and 1300 $^{\circ}\text{C}$, respectively. SBN+LN-0.2 samples show globular/irregular grains after sintering at 1100 $^{\circ}\text{C}$ and 1150 $^{\circ}\text{C}$ with grains sizes between 0.7–5.2 μm ($\bar{\varnothing}_{\text{li}} = 2.3(2) \mu\text{m}$) and 1–10 μm ($\bar{\varnothing}_{\text{li}} = 4.8(4) \mu\text{m}$). On the other hand, sintering at 1200 $^{\circ}\text{C}$ and 1300 $^{\circ}\text{C}$ leads to a change of the microstructure. After firing at 1200 $^{\circ}\text{C}$, we find a bimodal grain size distribution with irregular grains from 1.2 to 6 μm and few grains of about 8 μm . In addition small pillars with lengths between 1.5 and 4 μm and widths ranging from 3 to 19 μm as well as large rectangular micro crystals up to 200 μm were observed (Fig. S3, supporting information). After sintering at 1300 $^{\circ}\text{C}$ the ceramic bodies exclusively consist of pillars with dimensions similar to the ones after firing at 1200 $^{\circ}\text{C}$ and larger rectangular crystals with lengths up to 400 μm as shown in Fig. 5d.

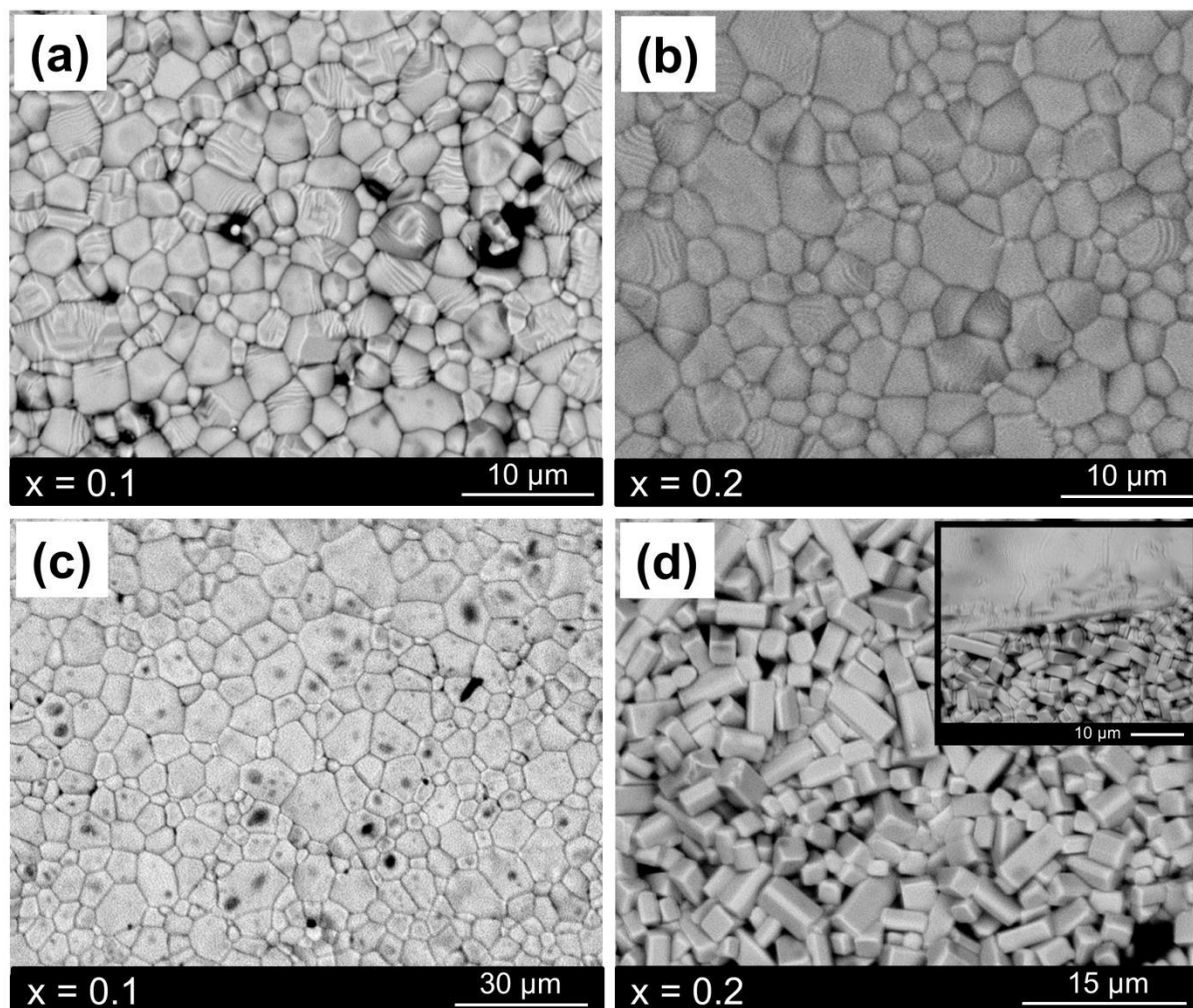


Fig. 5 SEM-BSE images of selected SBN+LN- x ceramic bodies sintered at different temperatures (T_s) for 1 h: (a) $T_s = 1150$ °C, (b) $T_s = 1150$ °C (c) $T_s = 1300$ °C, and (d) $T_s = 1300$ °C.

The phase composition after sintering was examined by XRD. Fig. 6 shows the XRD patterns of SBN+LN- x sintered ceramics. After sintering at 900 °C reflections of tetragonal $Sr_{0.5}Ba_{0.5}Nb_2O_6$, and traces of orthorhombic $SrNb_2O_6$ (JCPDS #00-028-1243) are observed. Additionally, the sample with $x = 0.2$ shows the presence of rhombohedral $LiNbO_3$. The $LiNbO_3$ and $SrNb_2O_6$ reflections disappear after sintering at 1000 °C for both $x = 0.1$ and 0.2, as visible in Fig. 6c and d. Up to the highest sintering temperature of 1300 °C the XRD

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patterns only show reflections of the $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ phase (Fig. 6e,f). Even a prolonged counting time of 10 s per step does not reveal any traces of secondary phases (Fig. S4, supporting information) suggesting the formation of a solid solution between $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ and LiNbO_3 in the tetragonal tungsten–bronze structure which will be the subject of further investigations. The proposed formation of a solid solution is additionally supported by the absence of the melting peak of LiNbO_3 around 1250 °C [44,45] in the DSC measurement as mentioned above. The solid solution can be written as $\text{Li}_y(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-y/2}\text{Nb}_2\text{O}_6$, where y represents the molar fraction of LiNbO_3 which can be calculated from the x parameter as $y = x/(1+x)$. Solid solutions between SBN and $(\text{K},\text{Na})\text{NbO}_3$ has been reported by several authors [46–48]. Because of the volatility of lithium salts at high temperatures, sintering often leads to a partial sublimation of Li_2O [49–51]. For our samples, atom absorption spectroscopy indicates that the loss of lithium accounts to about 6–7 % after sintering at 1300 °C for 1 h.

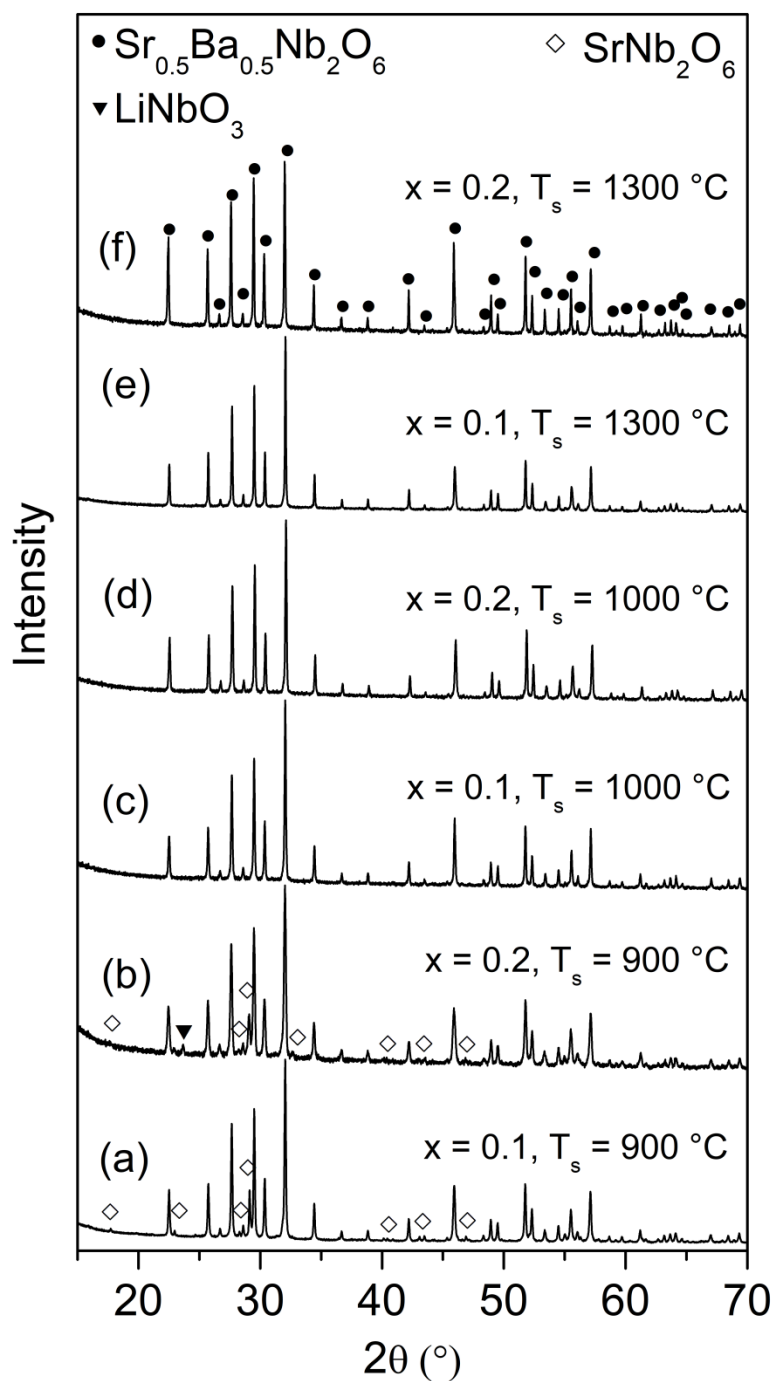


Fig. 6 Room-temperature XRD patterns of SBN+LN- x ceramics after sintering at different temperatures (T_s) for 1 h (heating-/cooling rate 5 K min^{-1}).

The optical band gap energies were obtained from diffuse reflectance spectra using the *Kubelka–Munk* theory. The optical band gap (E_g) can be described by equation (2) [52]:

$$F(R) \cdot h\nu = k(h\nu - E_g)^{1/n} \quad (2)$$

($F(R)$ – Kubelka–Munk function, k – energy-independent constant, E_g – optical band gap, n – exponent reflecting the type of transition with $n = 2$ for direct allowed transitions and $n = 0.5$ for indirect allowed transitions). As described elsewhere, $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ has an indirect band gap of 3.40–3.29 eV, depending on the sintering temperature [14,53]. Thus, E_g can be calculated by plotting of $(F(R) \cdot h\nu)^{0.5}$ versus $h\nu$ and extrapolating the slope to $F(R) \rightarrow 0$ (Fig. 7). Using this method, the band gap energies of SBN+LN- x ceramics with $x = 0.1$ were determined as 3.39(4) and 3.32(2) eV after sintering at 1100 and 1150 °C, whereas sintering at 1200 and 1300 °C gave values of 3.26(3) eV. However, in $x = 0.2$ ceramics, sintered above 1100 °C, an additional absorption feature appears at lower energies in the range between 2.4–3.1 eV, most likely caused by defects due the incorporation of Li^+ into the $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ structure [54–56]. Because of the overlapping of these two absorption regions, we used a baseline approach according to Makula et al. [55] to derive the band gap as seen in Fig. 7. The so obtained band gaps are 3.34(2) eV after sintering at 1100 °C and 3.36(6) eV for $x = 0.2$ samples sintered between 1150 and 1300 °C. As a conclusion, the use of the sintering additive LiNbO_3 does not lead to a considerable change of the band gap compared to pure $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ [14].

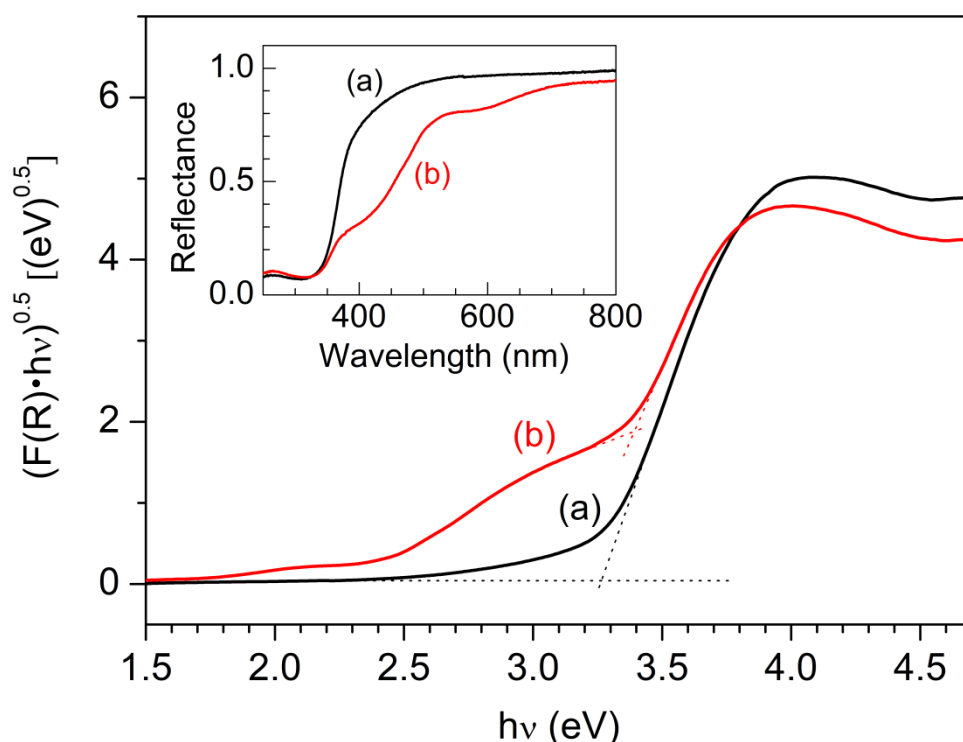


Fig. 7 $(F(R) \cdot h\nu)^{0.5}$ versus $h\nu$ of SBN+LN- x ceramics sintered at 1200 °C for 1 h. (a) $x = 0.1$, (b) $x = 0.2$. The inset shows the diffuse reflectance spectra.

3.1.3. Impedance spectroscopy

Fig. 8 shows the evolution of the relative permittivity (ϵ_r') and dissipation factor ($\tan \delta$) with temperature for ceramic bodies with $x = 0.1$ at 1 kHz. Samples fired at 1150, 1200, and 1300 °C show diffuse ferroelectric $\rightleftharpoons$ paraelectric phase transitions with broad maxima at 127(1), 117(1), and 118(1) °C, close to pure $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ [3,14]. The ϵ_r' values at these maxima increases with sintering temperature from 1362(123) to 3135(282) most likely caused by increasing grain sizes and densities. Fig. 9 shows the temperature (T_m) of the permittivity maxima depending on frequencies. T_m is shifted towards higher temperatures with increasing frequencies due to the relaxor-like behavior of the samples [57,58]. The shift of T_m in the

range from 1 kHz to 3 MHz is 6(2) K for the sample sintered at 1150 °C and increases to 11(2) K after sintering at 1300 °C (inset in Fig. 9).

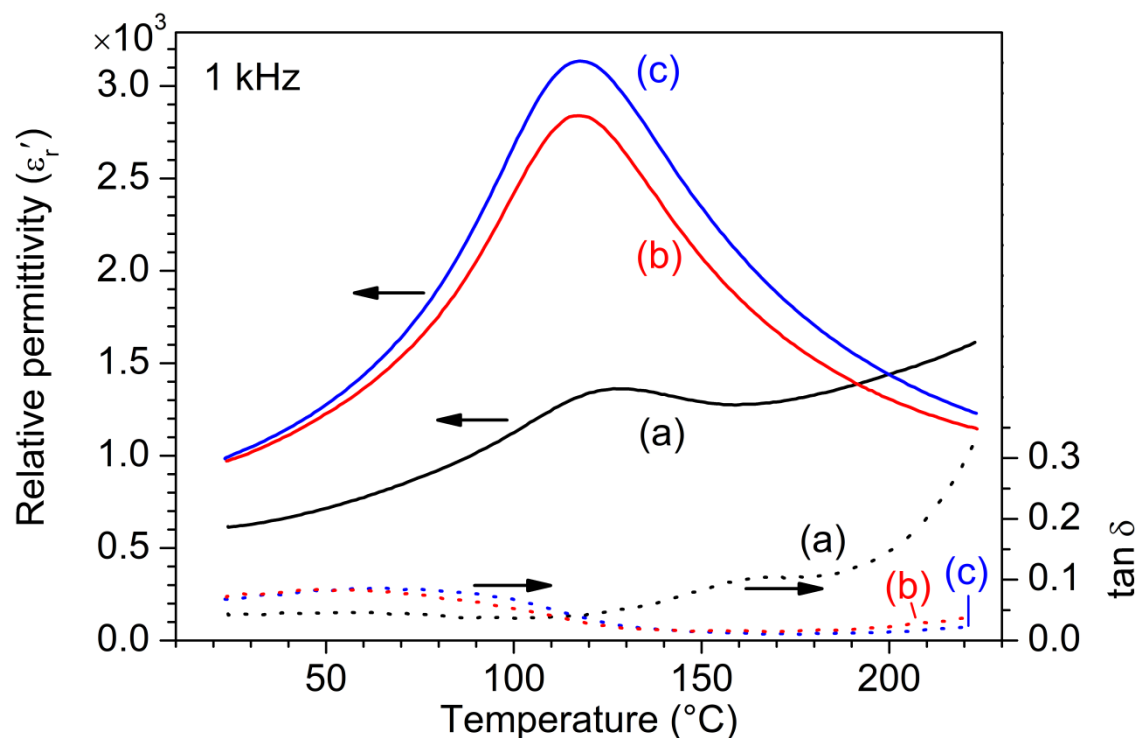


Fig. 8 Temperature dependence of the real part of the relative permittivity (ϵ_r') and $\tan \delta$ at 1 kHz of SBN+LN-0.1 ceramic bodies sintered for 1 h at: (a) 1150 °C, (b) 1200 °C, and (c) 1300 °C. The uncertainty of the data is smaller than the symbol size and is lower than 5 %.

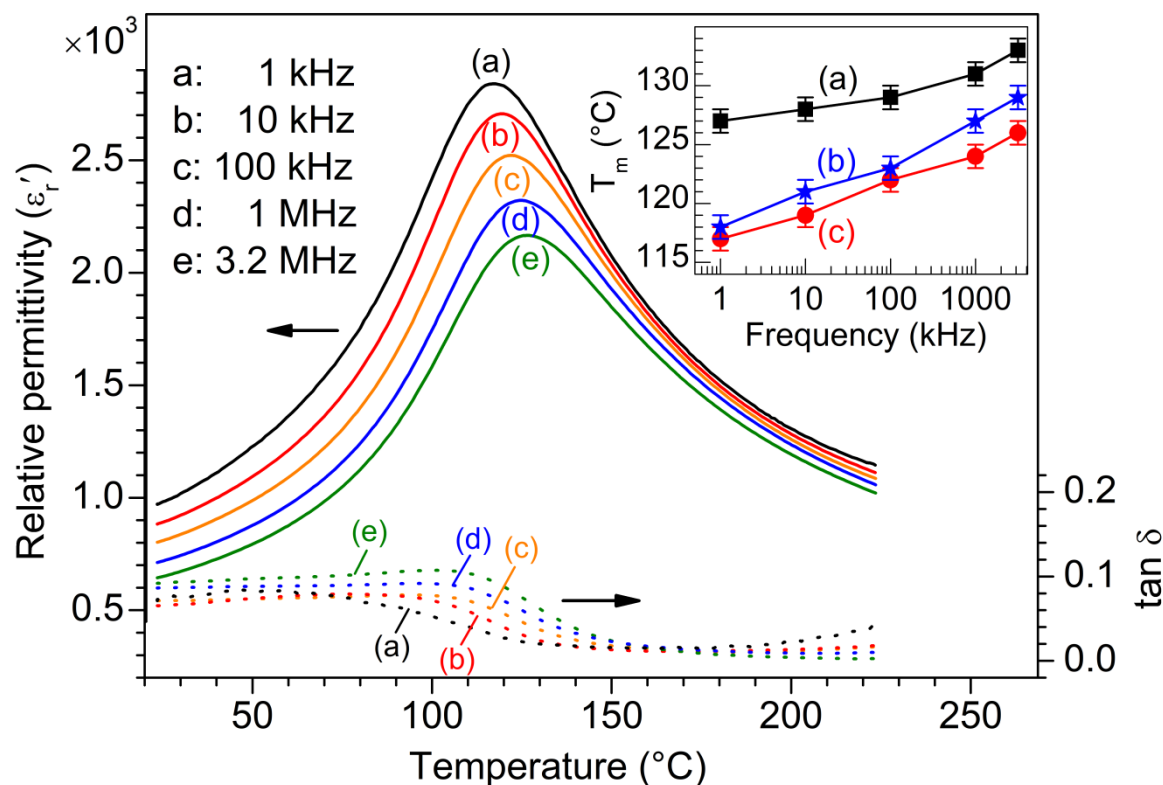


Fig. 9 Temperature dependence of the relative permittivity (ϵ_r') and the dissipation factor ($\tan \delta$) at various frequencies for SBN+LN-0.1 sintered at 1200 °C for 1 h. The inset shows the temperature of the permittivity maximum (T_m) depending on frequency and sintering temperature for samples sintered at: (a) 1150 °C, (b) 1200 °C, and (c) 1300 °C. The uncertainty of the data is smaller than the symbol size and is lower than 5 %.

The evolution of the permittivity depending on temperature for SBN+LN-0.2 ceramics can be seen in Fig. 10a. The samples with $x = 0.2$ show a shift of T_m towards higher temperatures. Sintering at 1100 °C does not lead to a clear phase transition at 1 kHz, whereas frequencies above 1 kHz reveal a maximum at 213(2) °C (Fig. 10b and Fig. S5, supporting information). The permittivity maximum of the dense ceramic, sintered at 1150 °C ($x = 0.2$), appears at 196(2) °C with $\epsilon_r' = 3071(277)$ at 1 kHz and shifts to 200(2) °C at 3 MHz with $\epsilon_r' =$

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2580(232) (Fig. S6, supporting information). The development of ϵ_r' for samples ($x = 0.2$) sintered at 1200 and 1300 °C shows only at frequencies ≥ 100 kHz a clear permittivity maximum at 223(2) and 221(2) °C corresponding to the diffuse ferroelectric $\rightleftharpoons$ paraelectric phase transition (Fig. S7 and S8, supporting information). Moreover, both the considerable shift of T_m to higher temperatures and the reduction of the permittivity maxima after sintering from 1150 to 1300 °C correlates with the appearance of a pillar-like microstructure as also observed in pure $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ [14]. Frequency-dependent dielectric measurements at room temperature (23 °C) in the range from 0.5 kHz to 10 MHz are shown in Fig. 11. The samples show decreasing permittivity values with rising frequency, while the dissipation factor ($\tan \delta$) slightly increases. The ϵ_r' values of the $x = 0.1$ ceramics (Fig. 11a) rise with sintering temperature caused by an increase in density and grain sizes. However, a different behavior can be observed for $x = 0.2$ ceramics (Fig. 11b). Sintering from 1100 to 1150 °C results in larger permittivities, while firing at 1200 and 1300 °C leads to significant lower ϵ_r' values, due to the change in microstructure after sintering at these temperatures as mentioned above. The ceramics sintered at 1200 °C ($x = 0.2$) consist of globular/irregular grains along with pillar-like grains which effects higher ϵ_r' values compared to those sintered at 1300 °C, which only show pillar-like grains. Decreasing permittivity values by changing from a globular/irregular to a pillar-like microstructure were also observed in $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ ceramics [14].

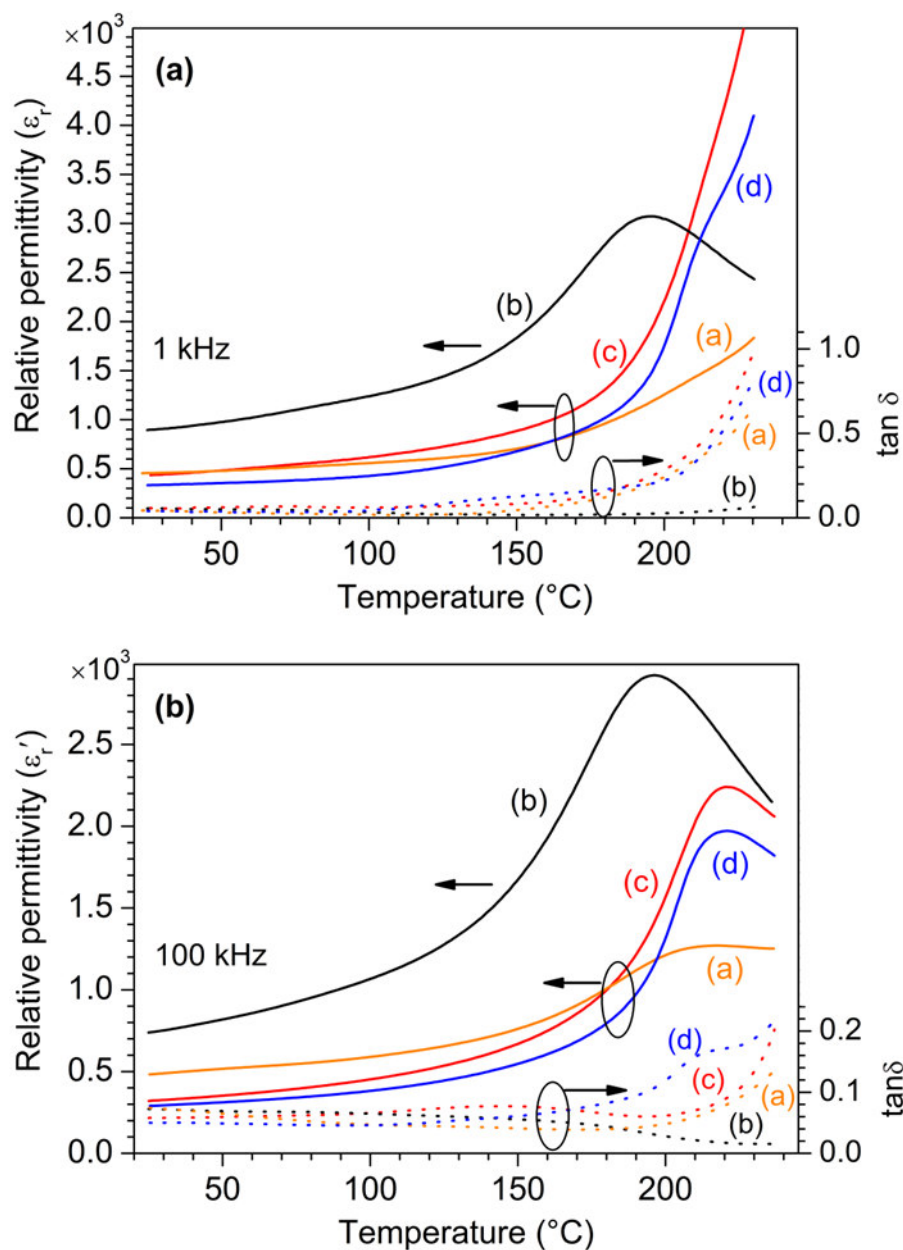


Fig. 10 Temperature dependence of the real part of ϵ_r' and $\tan \delta$ at 1 kHz (a) and 100 kHz (b) of SBN+LN-0.2 ceramic bodies sintered for 1 h at: (a) 1100 $^{\circ}\text{C}$, (b) 1150 $^{\circ}\text{C}$, (c) 1200 $^{\circ}\text{C}$ and (d) 1300 $^{\circ}\text{C}$. The uncertainty of the data is smaller than the symbol size and is lower than 5 %.

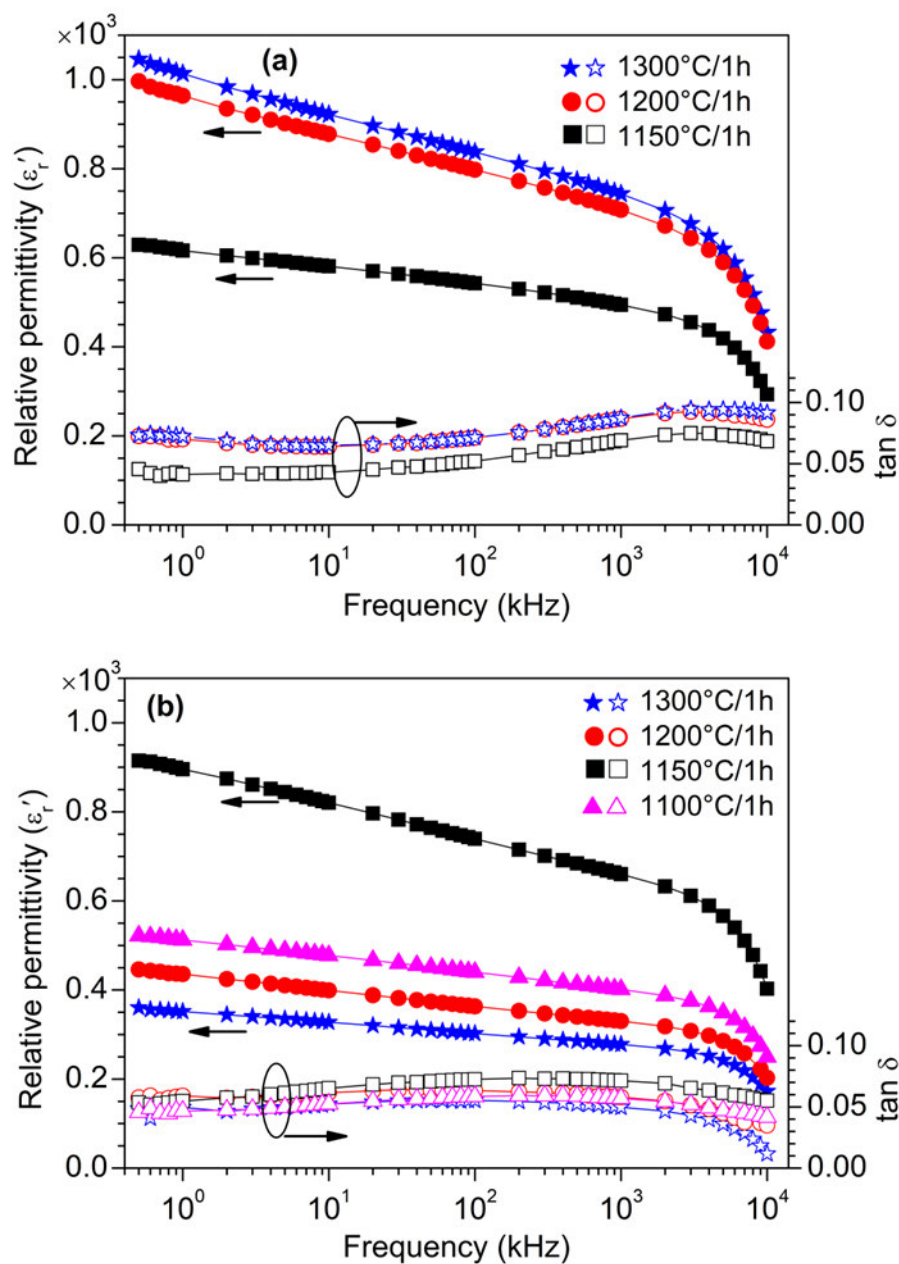


Fig. 11 Frequency dependence of the real part of ϵ_r' and the dissipation factor at 23 °C for SBN+LN- x ceramic bodies sintered at the indicated temperatures. **(a)** $x = 0.1$, **(b)** $x = 0.2$. The uncertainty of the data is smaller than the symbol size and is lower than 5 %.

The dielectric behavior of a relaxor ferroelectric can be expressed by the following Curie-Weiss type law (3) [59]:

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$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C'} \quad (3)$$

where, ε_m is the permittivity maximum, T_m is the temperature at ε_m , C' is a constant, and the exponent γ is the diffuseness coefficient. Thus, γ can be obtained from a plot of $\ln(\varepsilon^{-1} - \varepsilon_m^{-1})$ versus $\ln(T - T_m)$. $x = 0.1$ ceramics reveal diffuseness coefficients between 1.7–1.8, which is comparable with pure $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ [14], whereas $x = 0.2$ samples show a slightly larger γ value of 1.8–1.9. Larger γ values indicate an increasing degree of lattice disorder most likely due to formation of a solid solution between LiNbO_3 and $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ [60,61].

The discussion above is based on the model of a lossy capacitor and does not consider a possible dc-conductivity. At elevated temperatures the ceramics show considerable dc-conductivities suggesting a semiconducting nature. As reported elsewhere [62] for a single resistance-capacitor (RC) element, the specific impedance (ρ^*) is described by equation 4:

$$\rho^* = \frac{\rho_{dc}}{1 + (i\omega\tau)^\beta} \quad (4)$$

(β – constant phase shift (CPE) coefficient, $\tau = \rho_{dc}\varepsilon\varepsilon_0$). The high-temperature impedance data were modelled using equivalent circuits consisting of one or two parallel resistance-capacitor (RC) elements. For $x = 0.2$ ceramics sintered at 1200 and 1300 °C, the impedance data reveal two semicircle arcs, which can be described by two parallel connected RC-elements suggesting two different relaxation processes (Fig. 12). The two obtained relative permittivities for each of these ceramics are $13 \cdot 10^3$ and $27 \cdot 10^4$ sintered at 1200 °C, whereas values of $9 \cdot 10^3$ and $17 \cdot 10^4$ were found after sintering at 1300 °C. The smaller values can be related to bulk contributions, while the larger values most likely corresponds to grain boundary effects, as, according to Irvine et al. [63], the bulk permittivity is at least one order of magnitude lower than grain boundary permittivity. Cole-Cole plots for the other ceramic samples (Fig. S9 and Fig. S10, supporting information) show single semicircle arcs indicating

a single relaxation process. Because of the calculated permittivities between $1.6 \cdot 10^3$ and $3.5 \cdot 10^3$ these values can be assigned to the bulk effect, showing that grain boundary contributions play a negligible role in these samples.

Due to the addition of $LiNbO_3$, we observed an increase of the permittivity maximum up to 50 % and a considerable shift of T_m for $x = 0.2$, compared to pure $Sr_{0.5}Ba_{0.5}Nb_2O_6$ [14].

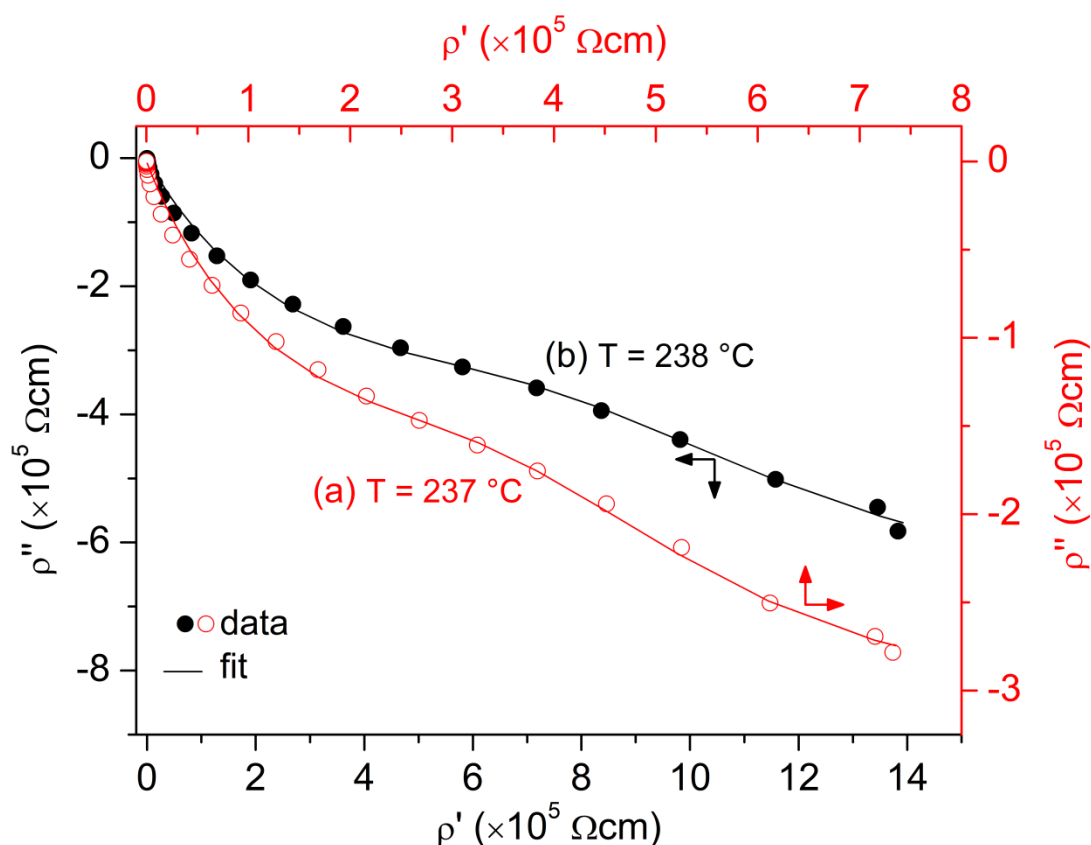


Fig. 12 Cole-Cole plots measured at the indicated temperatures of SBN+LN-0.2 ceramic bodies sintered for 1 h at (a) 1200 °C and (b) 1300 °C. Fits were carried out using two parallel connected RC-elements. Lines are the respective fit results, while symbols correspond to experimental data. The uncertainty of the data is smaller than the symbol size and is lower than 5 %.

4. Conclusion

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$\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ ceramics with the addition of 10 and 20 mol% LiNbO_3 as sintering aid were synthesized by a one-pot method using PEG400. Calcining at 600 °C results in white nanocrystalline powders with crystallite sizes of 31(3) and 29(3) nm and specific surface areas of 32(3) and 24(2) $\text{m}^2 \text{g}^{-1}$. Dilatometric measurements on powder compacts show that the sintering starts at significant lower temperatures with addition of LiNbO_3 . The activation energies for the initial stage of sintering were calculated as 300(18) and 271(15) kJ mol^{-1} for 10 and 20 mol% LiNbO_3 , respectively, while $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ without any sintering additive reveals an activation energy of 386(22) kJ mol^{-1} . Dense ceramic bodies were obtained after sintering at 1125 °C, which is about 200 K lower than for $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ ceramics without any sintering aid. XRD and DSC measurements indicate the incorporation of LiNbO_3 into the $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ structure by forming a solid solution during sintering. Temperature and frequency-dependent dielectric investigations show a diffuse ferroelectric $\rightleftharpoons$ paraelectric phase transition and a relaxor behavior. The dielectric maximum (T_m) slightly depends on the sintering temperature. T_m is around 120–130 °C for the addition of 10 mol% LiNbO_3 and shifts to about 200 °C for 20 mol%.

LiNbO_3 as sintering additive considerably reduced the sintering temperatures of $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ ceramics without the formation of a liquid phase. Due to the additive, the phase transition temperature (T_m) and the grain sizes can be easily tuned. LiNbO_3 is also a potential candidate as sintering aid in $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ based magnetoelectric composites.

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Appendix A. Supplementary data

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Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/>

Captions

Fig. 1

Room-temperature XRD patterns of SBN+LN- x ($= \text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6+x\text{LiNbO}_3$) powders after calcining at 600 °C for 2 h (heating rate 10 K min⁻¹): (a) $x = 0.1$, (b) $x = 0.2$. The insets show a magnification of the XRD pattern for $x = 0.1$ recorded with a prolonged counting time of 10 s per data point.

Fig. 2

Non-isothermal dilatometric measurements up to 1350 °C (heating rate 5 K min⁻¹) in flowing air of (a) SBN, (b) SBN+LN-0.1, (c) SBN+LN-0.2 of compacted powders calcined at 600 °C. The inset shows the shrinkage rates.

Fig. 3

Plot of $T^2[d(\Delta L L_0^{-1})dt]$ vs. $\Delta L L_0^{-1}$. For the sake of clarity, every 30th data point is marked by a symbol. Solid lines are the fit results.

Fig. 4

Bulk densities of ceramic bodies after sintering at various temperatures for 1 h (heating-/cooling rate 5 K min⁻¹).

Fig. 5

SEM-BSE images of selected SBN+LN- x ceramic bodies sintered at different temperatures (T_s) for 1 h: (a) $T_s = 1150\text{ }^{\circ}\text{C}$, (b) $T_s = 1150\text{ }^{\circ}\text{C}$ (c) $T_s = 1300\text{ }^{\circ}\text{C}$, and (d) $T_s = 1300\text{ }^{\circ}\text{C}$.

Fig. 6

Room-temperature XRD patterns of SBN+LN- x ceramics after sintering at different temperatures (T_s) for 1 h (heating-/cooling rate 5 K min^{-1}).

Fig. 7

$(F(R) \cdot h\nu)^{0.5}$ versus $h\nu$ of SBN+LN- x ceramics sintered at $1200\text{ }^{\circ}\text{C}$ for 1 h. (a) $x = 0.1$, (b) $x = 0.2$. The inset shows the diffuse reflectance spectra.

Fig. 8

Temperature dependence of the real part of the relative permittivity (ϵ_r') and $\tan \delta$ at 1 kHz of SBN+LN-0.1 ceramic bodies sintered for 1 h at: (a) $1150\text{ }^{\circ}\text{C}$, (b) $1200\text{ }^{\circ}\text{C}$, and (c) $1300\text{ }^{\circ}\text{C}$. The uncertainty of the data is smaller than the symbol size and is lower than 5 %.

Fig. 9

Temperature dependence of the relative permittivity (ϵ_r') and the dissipation factor ($\tan \delta$) at various frequencies for SBN+LN-0.1 sintered at $1200\text{ }^{\circ}\text{C}$ for 1 h. The inset shows the temperature of the permittivity maximum (T_m) depending on frequency and sintering

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temperature for samples sintered at: (a) 1150 °C, (b) 1200 °C, and (c) 1300 °C. The uncertainty of the data is smaller than the symbol size and is lower than 5 %.

Fig. 10

Temperature dependence of the real part of ϵ_r' and $\tan \delta$ at 1 kHz **(a)** and 100 kHz **(b)** of SBN+LN-0.2 ceramic bodies sintered for 1 h at: (a) 1100 °C, (b) 1150 °C, (c) 1200 °C and (d) 1300 °C. The uncertainty of the data is smaller than the symbol size and is lower than 5 %.

Fig. 11

Frequency dependence of the real part of ϵ_r' and the dissipation factor at 23 °C for SBN+LN- x ceramic bodies sintered at the indicated temperatures. **(a)** $x = 0.1$, **(b)** $x = 0.2$. The uncertainty of the data is smaller than the symbol size and is lower than 5 %.

Fig. 12

Cole-Cole plots measured at the indicated temperatures of SBN+LN-0.2 ceramic bodies sintered for 1 h at (a) 1200 °C and (b) 1300 °C. Fits were carried out using two parallel connected RC-elements. Lines are the respective fit results, while symbols correspond to experimental data. The uncertainty of the data is smaller than the symbol size and is lower than 5 %.

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Supporting Information

Effect of sintering additives on the densification and dielectric properties of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ ceramics synthesized by a soft-chemistry method

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The following abbreviations were used:

SBN+LF – $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6 + 0.76 \text{ LiF}$

SBN+LiN-0.1 – $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6 + 0.1 \text{ LiNbO}_3$

SBN+LiN-0.2 – $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6 + 0.2 \text{ LiNbO}_3$

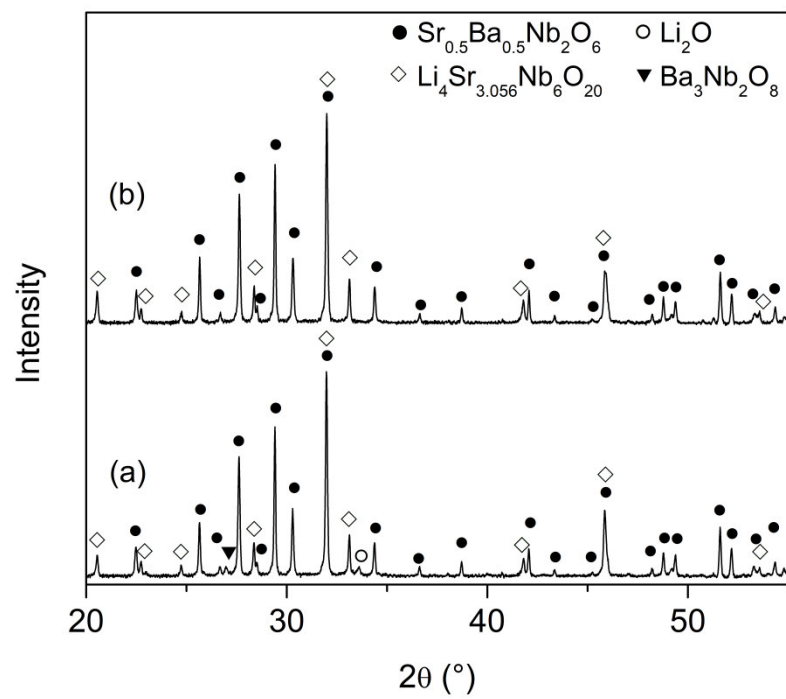


Fig. S1: Room-temperature XRD patterns of SBN-LF ceramics after sintering for 1 h at (a) 1050 °C, (b) 1200 °C.

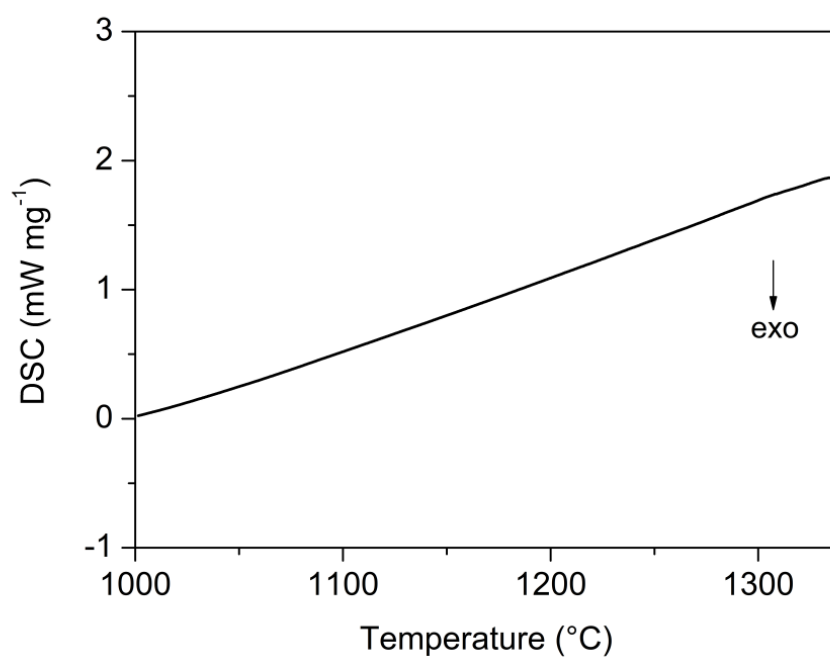


Fig. S2: DSC measurement of SBN+LN-0.2 compact in flowing air.

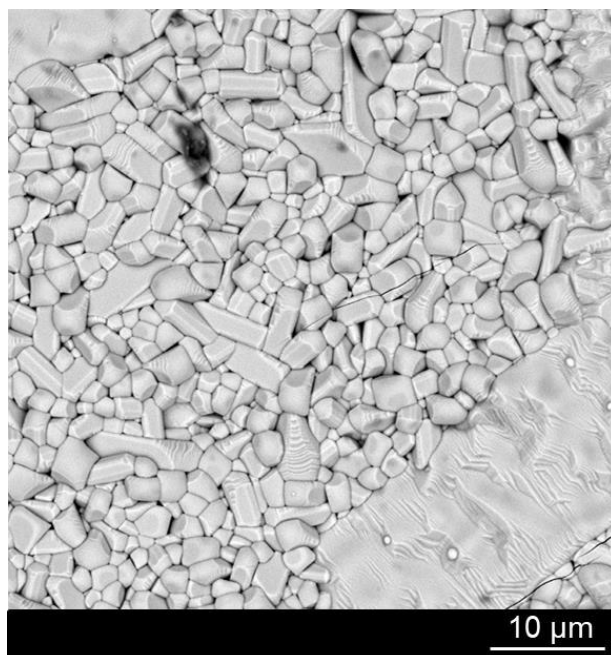


Fig. S3: SEM-BSE image of a SBN+LiN-0.2 ceramic body sintered at 1200 °C for 1 h.

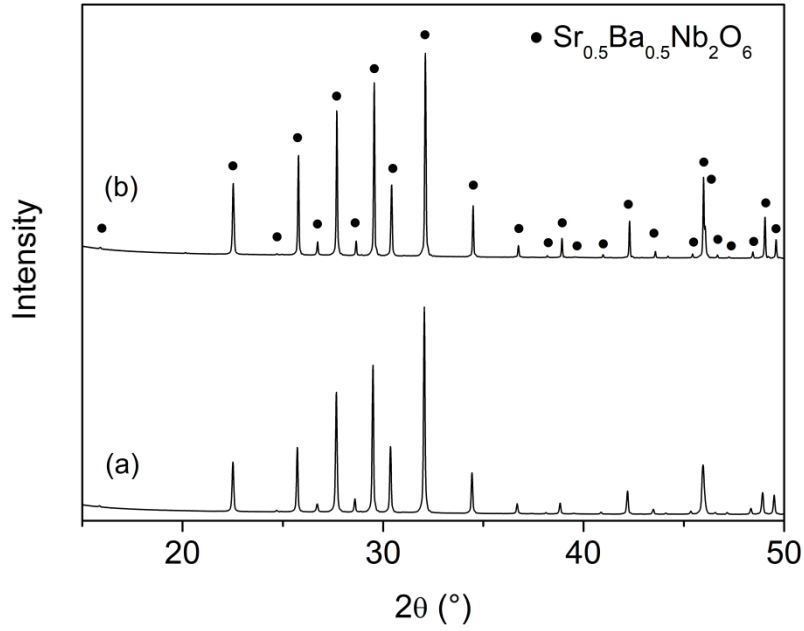


Fig. S4: Room-temperature XRD patterns of SBN+LN- x ceramics after sintering at 1300 °C for 1 h (heating-/cooling rate 5 K min⁻¹): (a) $x = 0.1$ (b) $x = 0.2$. The patterns were recorded with a prolonged counting time of 10 s per data point.

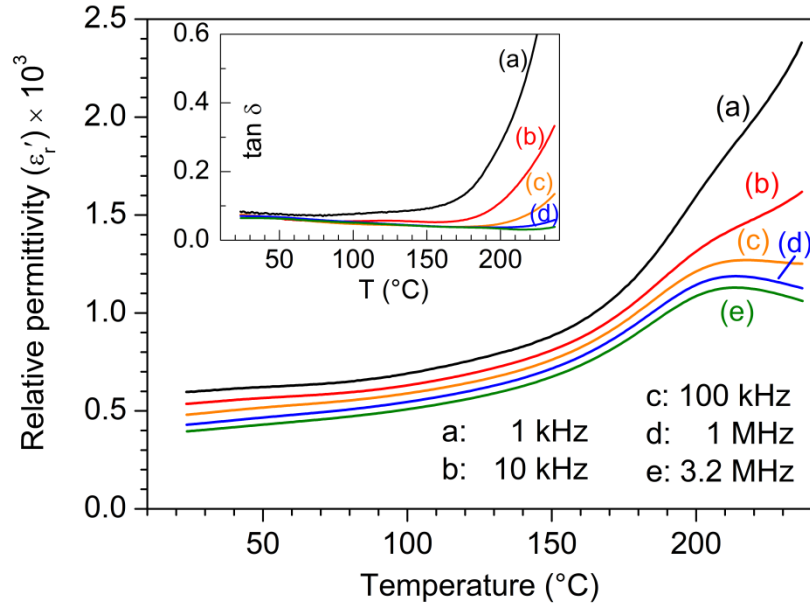


Fig. S5: Temperature dependence of ϵ_r' and $\tan \delta$ (inset) at various frequencies for a SBN+LN-0.2 ceramic body sintered at 1100 °C for 1 h.

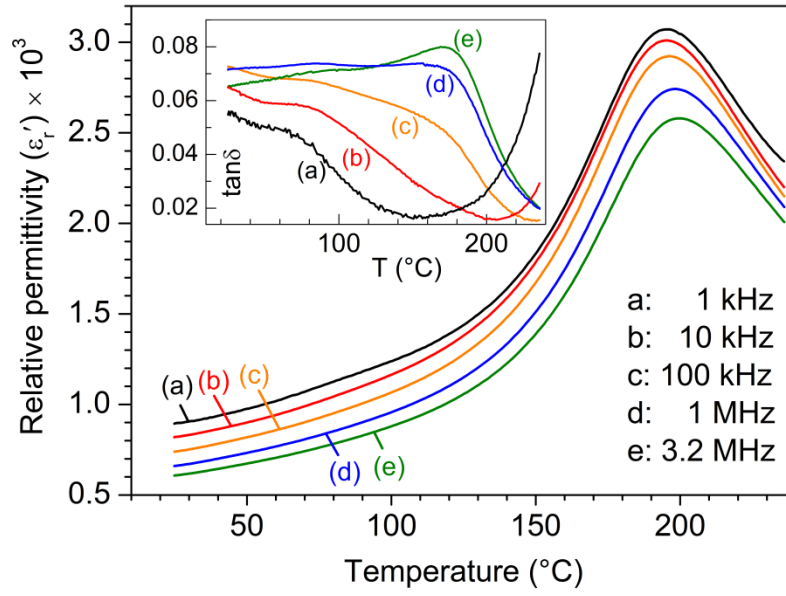


Fig. S6: Temperature dependence of ϵ_r' and $\tan \delta$ (inset) at various frequencies for a SBN+LiN-0.2 ceramic body sintered at 1150 °C for 1 h.

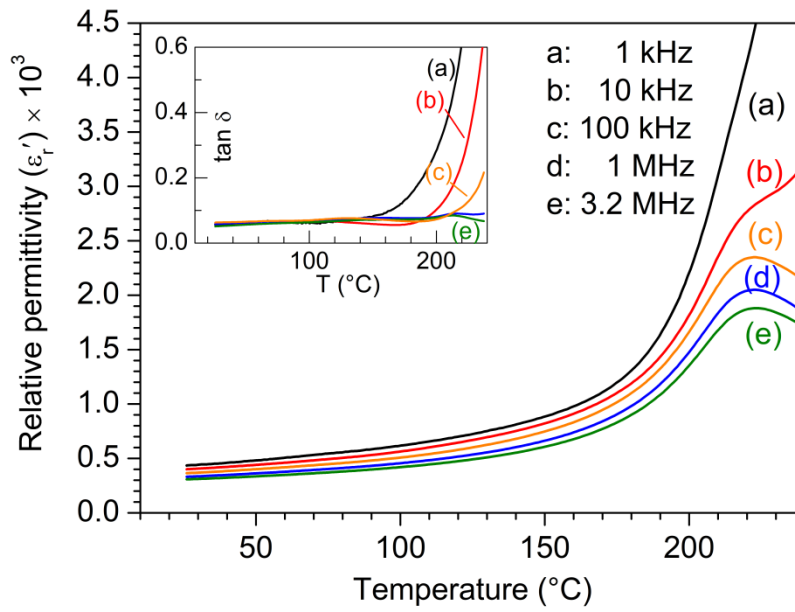


Fig. S7: Temperature dependence of ϵ_r' and $\tan \delta$ (inset) at various frequencies for a SBN+LiN-0.2 ceramic body sintered at 1200 °C for 1 h.

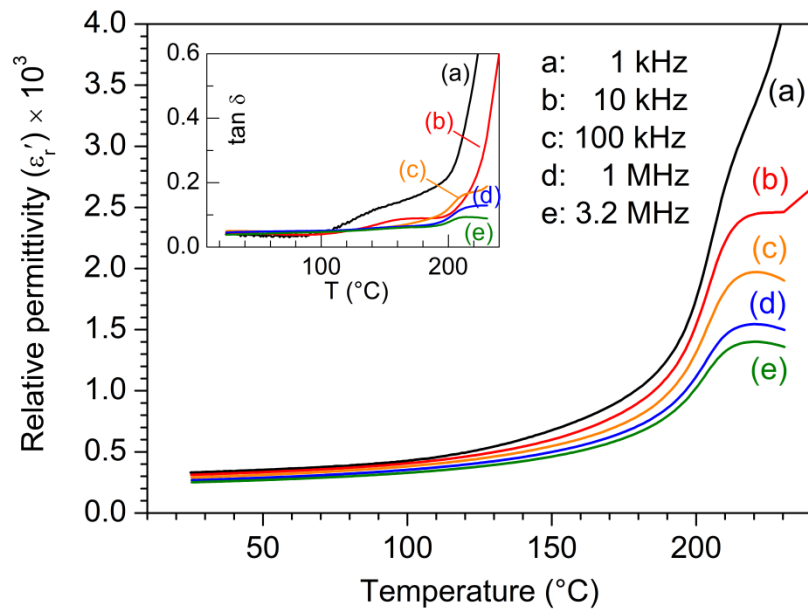


Fig. S8: Temperature dependence of ϵ_r' and $\tan \delta$ (inset) at various frequencies for a SBN+LiN-0.2 ceramic body sintered at 1300 °C for 1 h.

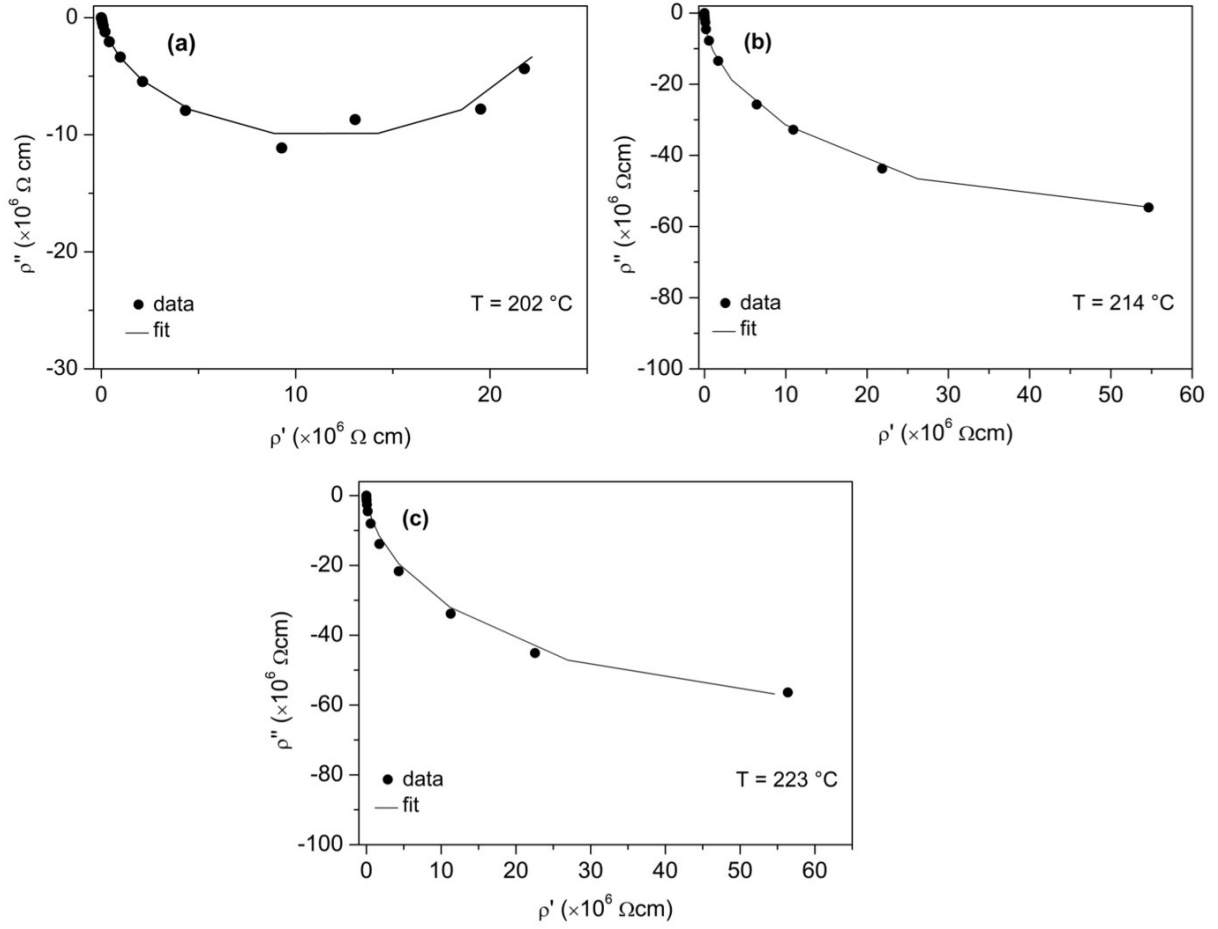


Fig. S9: Cole-Cole plots measured at the indicated temperatures of SBN+LiN-0.1 ceramics sintered for 1 h at different temperatures: (a) 1150 °C (b) 1200 °C, and (c) 1300 °C. Fits were carried out using one parallel connected RC-elements.

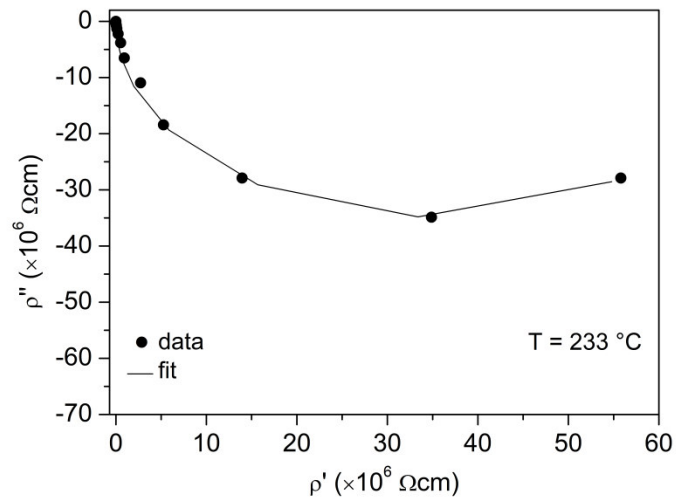


Fig. S10: Cole-Cole plot measured at the indicated temperature of SBN+LiN-0.2 ceramic sintered at 1150 $^{\circ}\text{C}$ for 1 h. The fit was carried out using one RC-elements.