

Impact of Li-substitution on dielectric, structural and sintering behavior of $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics

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Abstract. $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics were prepared by a solid state synthesis and sintered at 1300 °C. XRD investigations reveal single phase samples up to a substitution limit of $x = 0.275$. For higher lithium contents, the appearance of LiNbO_3 as secondary phase was observed. The density of the ceramics increases with lithium content. The microstructures show globular grains which turns to pillar-like grains with rising lithium substitution. Dielectric investigations confirm relaxor ferroelectric behavior and the diffuse phase transition is shifted towards higher temperatures with increasing lithium content from 129 °C ($x = 0$) to 221 °C ($x = 0.275$). The diffuseness coefficient increases with the lithium content. From high-temperature XRD measurements the length of the tetragonal cell parameter c decreases with increasing temperature, reaches a minimum at about 150–230 °C (depending on x) and afterward increases with increasing temperature. Additionally, a significant shift of the Nb(2) position with temperature can be observed.

Keywords: Strontium Barium Niobates, Niobates, Relaxor, Sintering, Dielectrics, Impedance spectroscopy

1. Introduction

Lead-free $\text{Sr}_y\text{Ba}_{1-y}\text{Nb}_2\text{O}_6$ based materials show excellent pyroelectric, piezoelectric, electro-optic, and photorefractive properties [1–3]. Additionally, strontium barium niobates can be used as catalyst in water splitting reactions and advanced oxidation processes [4–7]. $\text{Sr}_y\text{Ba}_{1-y}\text{Nb}_2\text{O}_6$ crystallized in the unfilled tetragonal tungsten bronze structure $[(\text{A}1)_{0.4}(\text{A}2)_{0.8}\text{C}_{0.8}(\text{B}1)_{0.4}(\text{B}2)_{1.6}\text{O}_6]$ which consists of corner-shared NbO_6 -octahedra (B1/B2) building tetragonal (A1), pentagonal (A2) and trigonal (C) channels along [001] (Fig. 1) [8,9]. The A1 sites (coordination number (CN): 12) are filled by Sr^{2+} , the A2 sites (CN: 15) are occupied both by Sr^{2+} and Ba^{2+} , while the smaller C sites (CN: 9) are empty. Additionally, 1/6 of the A1 and A2 sites are vacant [10,11]. The ferroelectric state in $\text{Sr}_y\text{Ba}_{1-y}\text{Nb}_2\text{O}_6$ is present in the range from $y = 0.25$ to 0.75 [12]. The ferroelectric properties depend on the composition (y) and the synthesis method. Relaxor behavior for polycrystalline $\text{Sr}_y\text{Ba}_{1-y}\text{Nb}_2\text{O}_6$ ceramics and single crystals has been reported for $y > 0.4$ [3,13–18]. The relaxor properties can be varied by partial ionic substitution on the A- and B-sites, respectively [19–21]. In relaxor materials the diffuse ferroelectric $\rightleftharpoons$ paraelectric phase transition extends over a temperature range (Curie range) and does not show a sharp transition in dielectric measurements in contrast to normal ferroelectric materials, therefore a well-defined Curie Temperature (T_C) does not exist. The diffuseness of the phase transition is due to the existence of polarized nano-regions in a paraelectric matrix even well above the temperature of the permittivity maximum (T_m) up to the so-called burns temperature (T_B)

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[22–24]. The diffuse phase transition (T_m) in $\text{Sr}_y\text{Ba}_{1-y}\text{Nb}_2\text{O}_6$ samples, lie between roughly 40 and 200 °C, depending on y [3,10,18,25,26]. Moreover, the dielectric response, sintering behavior, and microstructure of $\text{Sr}_y\text{Ba}_{1-y}\text{Nb}_2\text{O}_6$ ceramics can be varied by partial substitution of $\text{Sr}^{2+}/\text{Ba}^{2+}$ by e.g. alkaline metal ions [21,27–31]. Recently, we have found a considerably increase in density and of the magnetoelectric coefficient in $\text{NiFe}_2\text{O}_4\text{--Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ composites due to the partial replacement of $\text{Sr}^{2+}/\text{Ba}^{2+}$ by Li^+ [32]. However, systematic investigations on the influence of lithium substitution on the dielectric, structural and sintering behavior of strontium barium niobate have not been reported.

The aim of this work is to investigate the impact of the lithium content in $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ on the ferroelectric, structural, and sintering behaviour up to the substitution limit. The specimens were obtained from a conventional solid state synthesis. Phase evolution and microstructure of the ceramics were monitored by XRD and SEM. Dielectric and diffuse reflectance UV-Vis measurements were used to determine the influence of lithium on the phase transition temperature and optical band gap, respectively. High-temperature XRD measurements reveal the structural change during the phase transition.

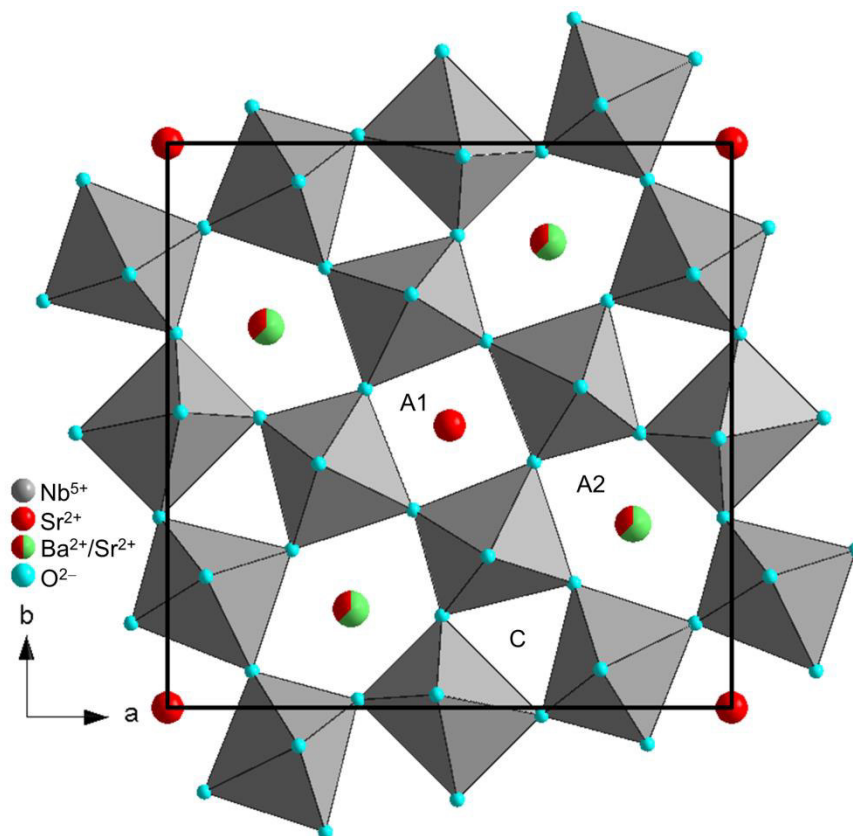


Fig. 1. The tetragonal tungsten bronze structure of strontium barium niobate viewed along [001].

2. Experimental

2.1. Material preparation

$\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ($\equiv (\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6)_{1-x/2}(\text{LiNbO}_3)_x$ solid solution) ceramic samples were prepared by a solid state synthesis. Stoichiometric amounts of Nb_2O_5 (abcr, 99.995%), BaCO_3 (Alfa Aesar, Puratronic, 99.997%), SrCO_3 (Alfa Aesar, Puratronic, 99.994%), and Li_2CO_3 (Acros Organics, 99.999%) were mixed in polyamide jars for 4 h using a planetary mill, ZrO_2 -balls, and propan-2-ol. After drying the mixtures were calcined in static air between 1200–1250 °C for 3–5 h to ensure complete calcination (Fig. S1, supporting information). The white calcined powders were then mixed with 10 wt% of a saturated aqueous polyvinyl alcohol (PVA) solution as a pressing aid and uniaxially pressed at about

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110 MPa into pellets (green density: 3 g cm^{-3}). These pellets were placed on a ZrO_2 fibre mat and fired to ceramic bodies at 1300°C for 1 h (heating-/cooling rate 5 K min^{-1}).

2.2. Characterization

Room-temperature X-ray powder diffraction were carried out on a Bruker AXS D8-Advance diffractometer, equipped with a one-dimensional silicon strip detector (LynxEye™) using Cu-K_α radiation in the range of $2\theta = 10\text{--}140^\circ$ with a step size of 0.0105° and a counting time of 1 s per data point. Temperature dependent XRD measurements were conducted on a STOE STADI MP diffractometer with monochromatic $\text{Mo-K}_{\alpha 1}$ radiation equipped with a DECTRIS MYTHEN2 1K detector and a STOE HT1 capillary furnace. Samples were contained in 0.8 mm external diameter capillaries, and the temperature range of 50 to 300°C was scanned in steps of 10°C . Diffraction patterns were obtained in the range of $2\theta = 5\text{--}51^\circ$ with a point resolution of 0.015° and a total acquisition time of 2 h. Rietveld refinements were carried out with the software FullProf [33]. Scanning electron microscope images were collected with a Phenom ProX SEM in backscattered electron mode (BSE). An Impedance Analyzer 4192A (Hewlett Packard) was used for impedance measurements. For this purpose, ceramic samples were sputtered on both sides with 100 nm thick gold electrodes using a Cressington Sputter Coater 108auto. Diffuse reflectance spectra were recorded at room temperature using a Perkin Elmer UV–Vis spectrometer Lambda 19 with BaSO_4 as white standard.

3. Results and discussion

3.1. Phase composition, sintering and optical band gap

The preceramic powders were pressed to pellets and sintered in static air at 1300°C for 1 h (heating-/ cooling rate: 5 K min^{-1}) to ceramic bodies which were used for further

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investigations. Fig. 2 shows room-temperature XRD patterns of $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramic samples depending on the lithium content (x). Up to $x = 0.275$ we observed only reflections of the tetragonal (SG: $P4bm$) $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ phase (PDF #01-084-4102), without any traces of a secondary phase, like e.g. LiNbO_3 , 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 yielding $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ in the tetragonal tungsten bronze structure. On the other hand, the formation of a weak LiNbO_3 reflection (PDF #01-078-0250) at about $2\theta = 23.7^\circ$ for $x = 0.3$ indicates a solution limit at about $x = 0.275$. Rietveld refinements in space group $P4bm$ [10,11] (Fig. S2, supporting information) show a decrease of both lattice parameters with increasing lithium content (Fig. 3), because of the smaller ionic radius of Li^+ compared to Sr^{2+} and Ba^{2+} [34]. The contraction with rising x of the shorter c -axis up to 0.46(1) % is significantly greater than that of the a -axis (up to 0.21(1) %) (Fig. S3, supporting information).

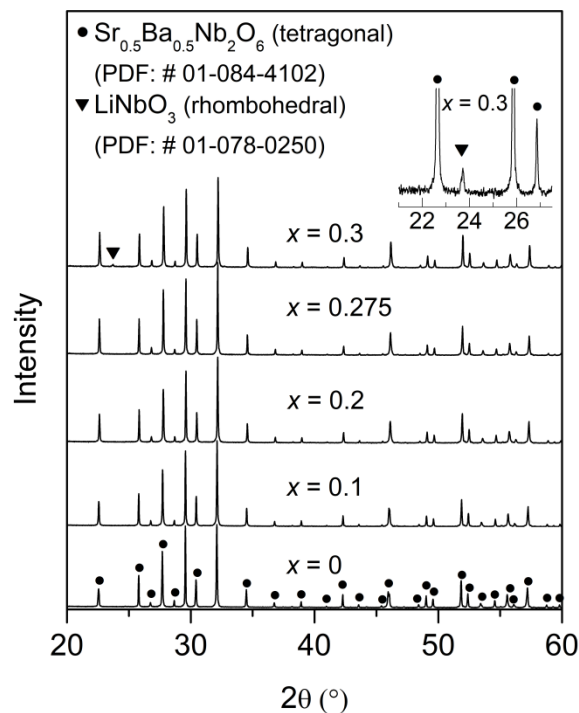


Fig. 2. Room temperature XRD patterns of $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics sintered at 1300 °C for 1 h. The inset shows a magnification of the pattern for $x = 0.3$.

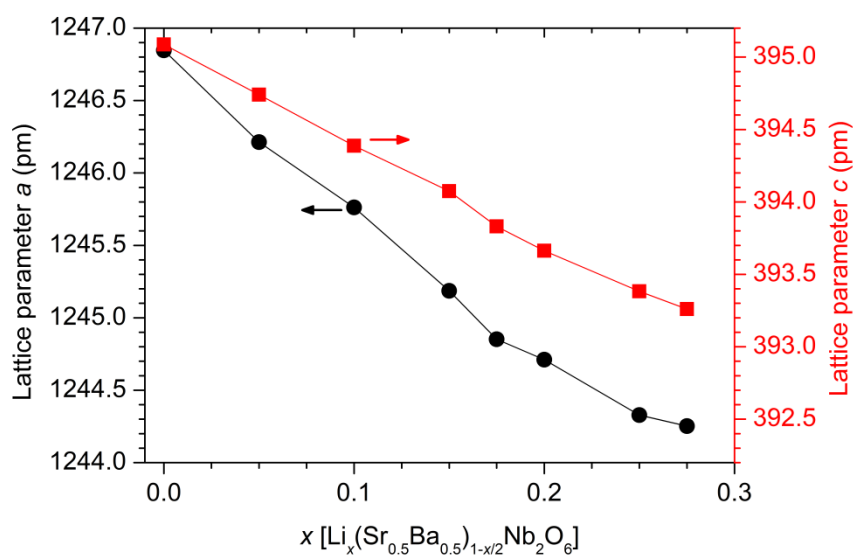


Fig. 3. Evolution of the tetragonal lattice parameters of $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ depending on the lithium content (x) at room temperature. The uncertainties of the data are smaller than the symbol size.

The bulk densities of the white ceramic bodies were calculated from their weight and geometric dimension. The relative bulk densities were related to the theoretical (single crystal) densities (Tab. S1, supporting information) [16,35–37]. As seen in Fig. 4, the densities of the $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramic bodies increase with increasing lithium content (x). The slight drop in density for $x > 0.2$ is most likely due to the formation of a mainly pillar-like microstructure (see below) [29].

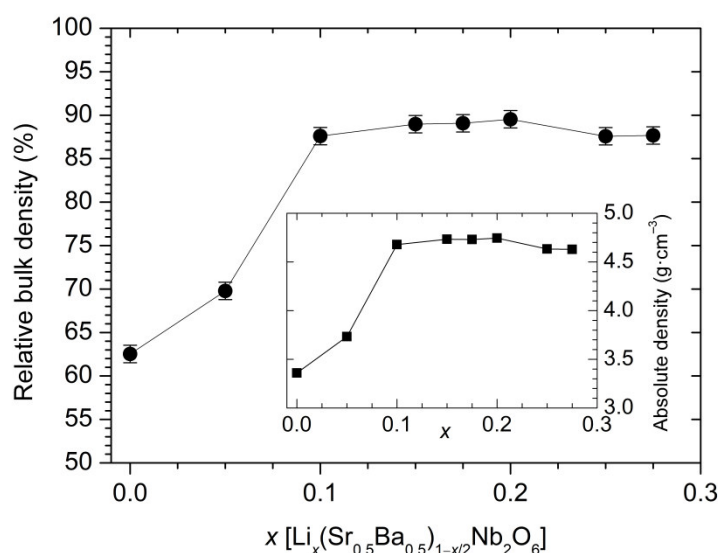


Fig. 4. Relative bulk densities of ceramic bodies in dependence of x after sintering at 1300 °C for 1 h (heating-/cooling rate 5 K min⁻¹). The inset shows the absolute bulk densities. The uncertainties of the data in the inset are smaller than the symbol size.

SEM (BSE mode) images of the microstructure of selected ceramics are shown in Fig. 5 (see also Fig. S4, supporting information). After sintering, samples up to a lithium substitution level of $x < 0.15$ consist only of globular and irregular shaped grains, respectively. The average grain size ($\bar{\phi}_{\text{li}}$) of those grains was determined by counting of at least 1000 grains per sample using the lineal intercept method [38]. The globular-/irregular grains grow from 1.5–14 μm ($\bar{\phi}_{\text{li}} = 6.7(3) \mu\text{m}$) for $x = 0$ to 2.2–26 μm ($\bar{\phi}_{\text{li}} = 10(1) \mu\text{m}$) for $x = 0.15$. The grain size range represents the smallest and largest grains in the sample. Besides these globular

grains, we also observed the appearance of pillar-like grains and large crystals at $x \geq 0.15$. At a lithium level of $x = 0.15$ the pillar-like grains have dimensions of about $4\text{--}8 \times 6\text{--}16 \text{ }\mu\text{m}$. For $x = 0.25$ the pillars grow to $4\text{--}14 \times 5\text{--}50 \text{ }\mu\text{m}$ along with the appearance of sporadic large grains up to $50 \times 170 \text{ }\mu\text{m}$, whereas the globular-/irregular grains have dimensions of about $4\text{--}83 \text{ }\mu\text{m}$ ($\bar{\phi}_{\text{li}} = 16(3) \text{ }\mu\text{m}$). The fraction of the pillar-like grains and large grains increases considerably with x , therefore for $x = 0.275$ the microstructure of the ceramic sample completely consists of pillars between $3\text{--}25 \times 5\text{--}74 \text{ }\mu\text{m}$ and large grains up to $50 \times 125 \text{ }\mu\text{m}$ (Tab. S2, supporting information). Thus, the incorporation of Li^+ promotes an anisotropic grain growth resulting in the formation of pillar-like grains and abnormal grain growth, which was also observed in potassium and sodium substituted calcium/strontium barium niobates as well as in $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ ceramics fired at high temperatures [17,21,28,39]. According to Lee et al. [20,40] the formation of pillar-like and especially large grains is most likely caused by a stoichiometry gradient between grain and grain-boundary leading to Nb_2O_5 - and probably lithium-rich grain-boundary regions with a locally reduced melting point.

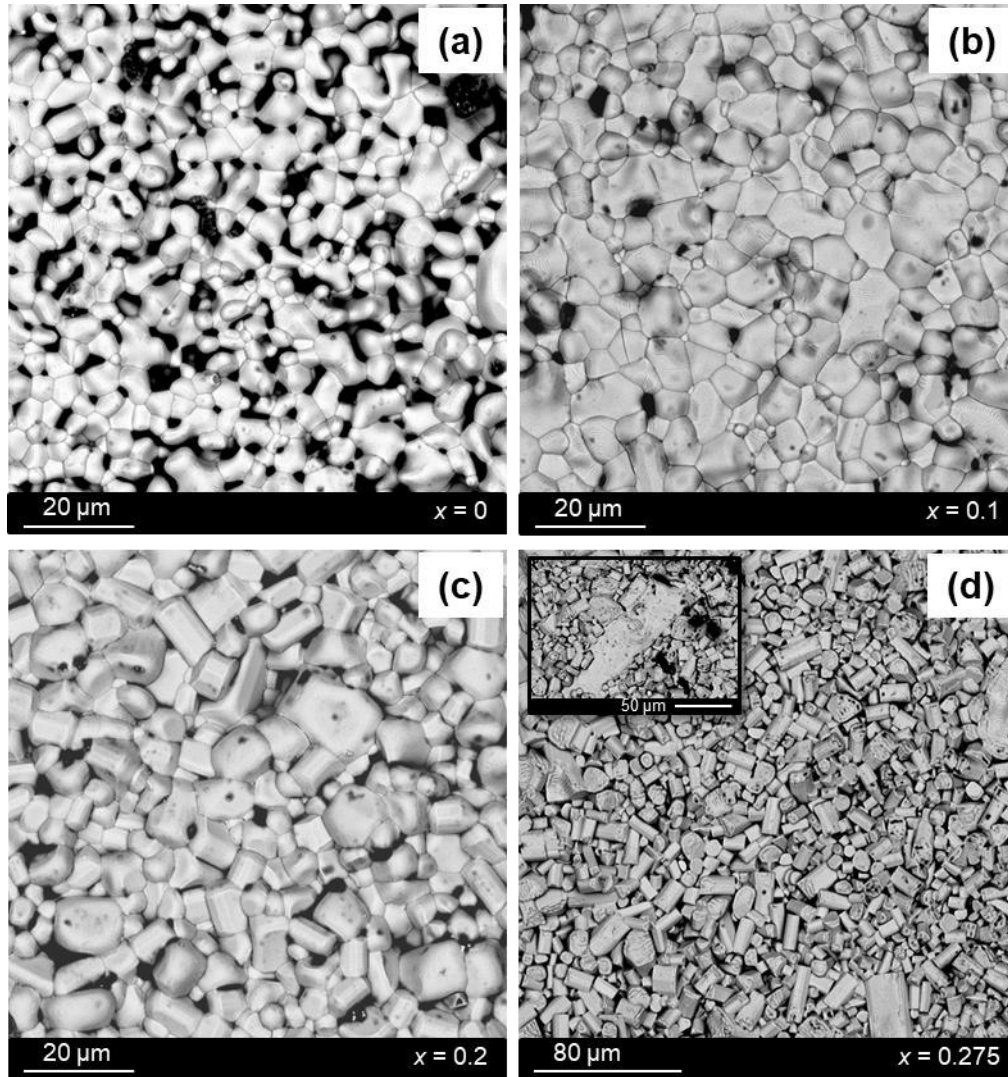


Fig. 5. SEM-BSE images of selected $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramic bodies sintered at 1300 °C for 1 h. a) $x = 0$, b) $x = 0.1$, c) $x = 0.2$, d) $x = 0.275$. The inset in (d) shows a very large irregular grain.

From diffuse reflectance UV-Vis spectra (Fig. S5, supporting information) we obtained the optical band gap energies of the samples applying the Kubelka-Munk theory. For that purpose, the measured reflectance data (R) were converted into the absorption coefficient (α). Assuming the scattering factor (s) is wavelength independent α is proportional to the Kubelka-Munk function $F(R)$ as given by equation 1 [41–43]:

$$F(R) = \frac{\alpha}{s} = \frac{(1-R)^2}{2R} \quad (1)$$

The optical band gap can be calculated by equation 2 [41]:

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

where, k – energy-independent constant, E_g – optical band gap, n – exponent reflecting the type of transition. As described elsewhere, $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ has an indirect band gap, thus the exponent is set to $n = 0.5$ [17,44]. Generally, the band gap energy can be estimated from a plot of $(F(R) \cdot h\nu)^{1/2}$ versus $h\nu$ and extrapolating the slope to $F(R) \rightarrow 0$. However, an additional absorption feature appears at lower energies most likely caused by defects in the crystal structure [45–47]. Because of the overlapping of these two absorption regions, we used a baseline approach to determine E_g according to Makula et al. [47] as seen in the inset of Fig. 6. The obtained band gap energy of 3.33(3) eV for $x = 0$ agrees very well with previous values for $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ [17,48]. Moreover, it can be seen in Fig. 6 the incorporation of Li^+ into the $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ lattice does not change the band gap energy significantly.

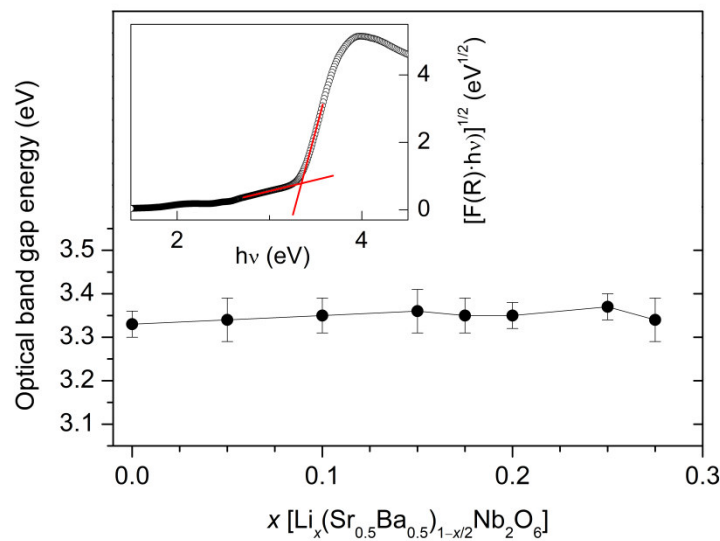


Fig. 6. Optical band gap energies (indirect allowed) of $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics sintered at 1300 °C for 1 h. The inset exemplarily shows $(F(R) \cdot h\nu)^{1/2}$ versus $h\nu$ for a ceramic sample with $x = 0.2$.

3.2. Dielectric and High-temperature XRD measurements

The temperature-dependence of the relative permittivity (ϵ_r') and dissipation factor ($\tan\delta$) for $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramic bodies at 1 MHz is shown in Fig. 7. The temperature of the permittivity maximum (T_m) is shifted towards higher temperatures with x from 129(3) °C ($x = 0$) to 221(4) °C ($x = 0.275$) (Fig. 8). $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ is a relaxor ferroelectric and the broad permittivity maximum suggests a diffuse ferroelectric $\rightleftharpoons$ paraelectric phase transition. Additionally, T_m of the $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ samples shifts towards higher temperatures with increasing frequency (Fig. S6, supporting information). Li^+ preferably occupies the C site, however Li^+ can also occupy the A1 and A2 sites [49]. As pointed out by Abrahams et al. [50] the temperature of the dielectric maximum depends on the displacement of the Nb^{5+} ions inside the oxygen octahedra. Thus, the incorporation of Li^+ leads to an increase of the octahedron distortion and Nb^{5+} displacement resulting in rising T_m values with x . Additionally, we also observe an increase of the permittivity maximum up to a lithium

substitution of $x = 0.175$ – 0.2 . The same trend is true for the permittivity values at room temperature (inset in Fig. 8). The low permittivity values for ceramics with $x = 0$ and 0.05 are also a consequence of the lower bulk densities and thus higher porosity [51]. The observed significant drop of the permittivity maximum for samples with $x > 0.2$ gets along with the formation of a mainly and complete pillar-like microstructure, respectively. Since a decrease of the permittivity maximum upon formation of a pillar-like microstructure was also observed in pure $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ ceramics [17] we suppose that the significant change in microstructure connected with the formation of new grain boundaries is most likely the main reason for the decrease of the dielectric response.

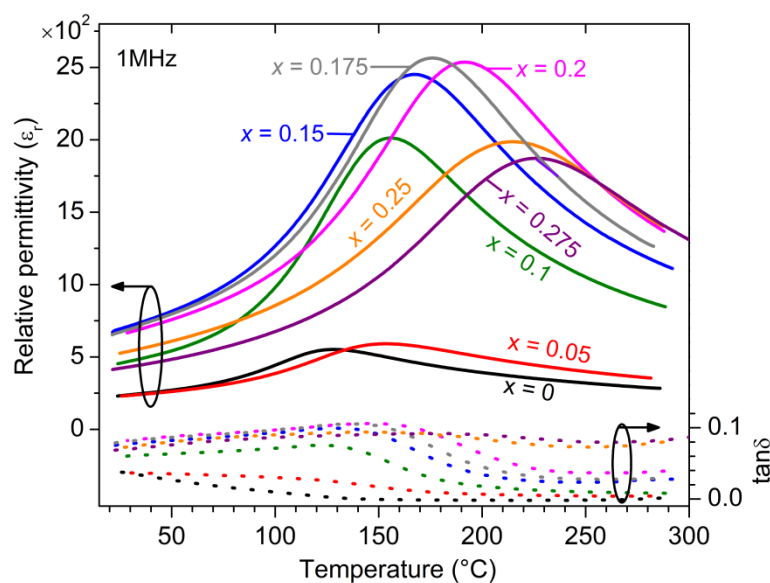


Fig. 7. Temperature dependence of the relative permittivity (ϵ_r) and dissipation factor ($\tan \delta$) at 1 MHz for $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics sintered at 1300 °C.

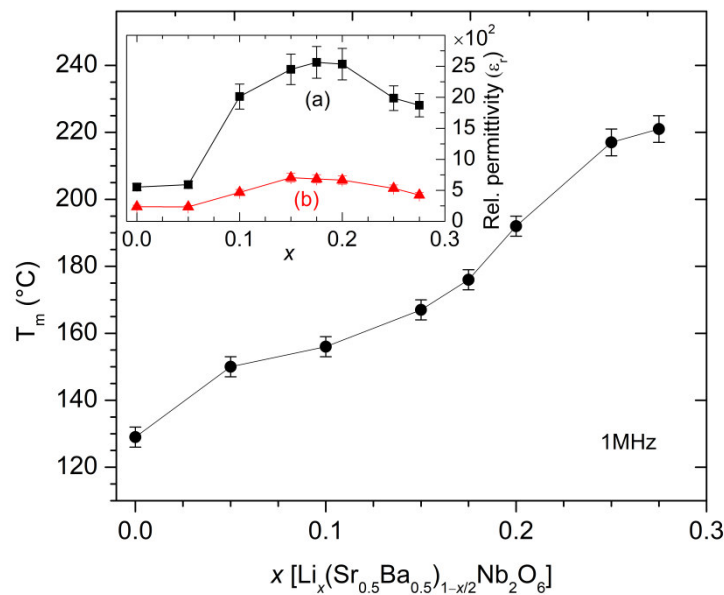


Fig. 8. Evolution of the temperature of the permittivity maximum (T_m) depending on the composition x at 1 MHz. The inset shows the permittivity values depending on x at T_m (a) and at room temperature (b).

The dielectric behavior of a relaxor ferroelectric can be expressed by the modified Curie-Weiss law (3) [52]:

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

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. γ can be derived from a plot of $\ln(\varepsilon^{-1} - \varepsilon_m^{-1})$ versus $\ln(T - T_m)$ (Fig. S7, supporting information). It is commonly assumed that $\gamma = 1$ for a normal ferroelectric material and $\gamma = 2$ for an ideal relaxor ferroelectric one. The derived diffuseness coefficient rises from 1.63(5) ($x = 0$) to 1.94(5) ($x = 0.275$) (Fig. 9) indicating an increase of the diffuse nature of the phase transition caused by an increase of lattice disorder with rising lithium content [53,54].

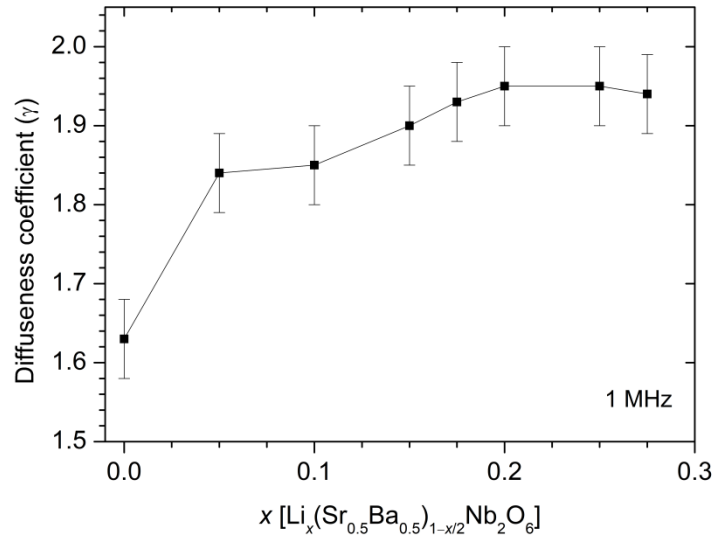


Fig. 9. Diffuseness coefficient versus lithium content (x) for ceramic samples sintered at 1300 °C.

At higher temperatures, the $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics reveal a considerable dc-conductivity indicating a semiconducting behavior. In contrast, the ceramics samples show low conductivities at room temperature ($\sigma_{\text{DC}} \ll 10^{-8} \text{ S cm}^{-1}$), thus the high-temperature impedance data were fitted with an equivalent circuit consisting of one resistance-capacitor (RC) element including a constant phase-shift element. The specific complex impedance (Z_{spec}^*) for a single RC element is described by equation 4[55]:

$$Z_{\text{spec}}^* = \frac{\rho_{\text{DC}}}{1 + (i\omega\tau)^\beta} \quad (4)$$

(β is the constant phase-shift (CPE) coefficient, ρ_{DC} is the specific DC resistivity, and $\tau = \rho_{\text{DC}}\epsilon\epsilon_0$). Cole-Cole plots of the specific impedance of the samples can be successfully described by one RC element (Fig. S8, supporting information). The calculated specific DC resistivities (ρ_{DC}) of the specimen up to about $x = 0.2$ is one magnitude higher than the one of unsubstituted $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ samples. However, for higher lithium levels ($x > 0.2$) the

resistivity values decrease significantly (Fig. 10), which correlates with the change in microstructure from globular-like to pillar-like grains (see above) .

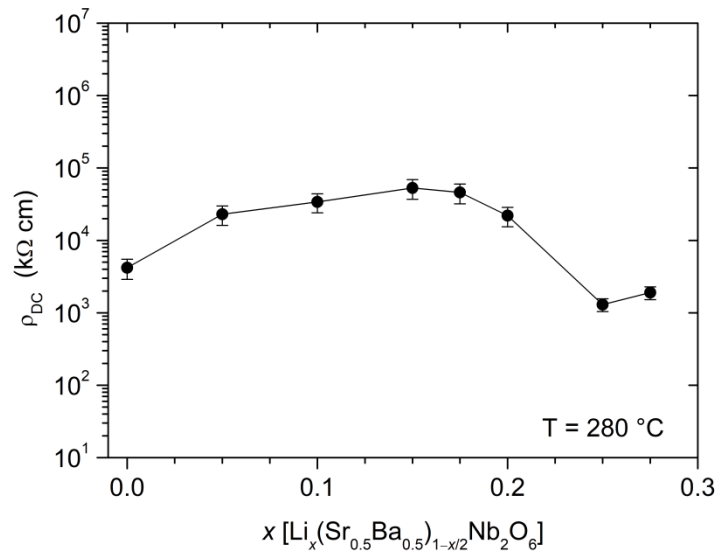


Fig. 10. Development of the specific DC resistivity with lithium content (x) of $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics.

We carried out temperature dependent XRD measurements to examine the evolution of the cell parameters during the diffuse transition from the ferroelectric to the paraelectric phase. Fig. 11 shows the relative length change, related to the initial values at 50 °C, of the cell parameters with temperature. All samples reveal a similar behavior. The lattice parameter a (Graph 11a) increases almost linearly with temperature due to the expected thermal expansion. The shorter c -axis (Graph 11b) shows a completely different behavior. The lattice parameter c decreases with temperature, reaches a minimum and afterwards c increases. The minimum tends to shift to higher temperatures with increasing lithium substitution (x) analogous to the dielectric maximum (T_m) described above. The positive temperature coefficient of c at high temperatures is mainly dominated by the expected increasing atomic oscillation with temperature.

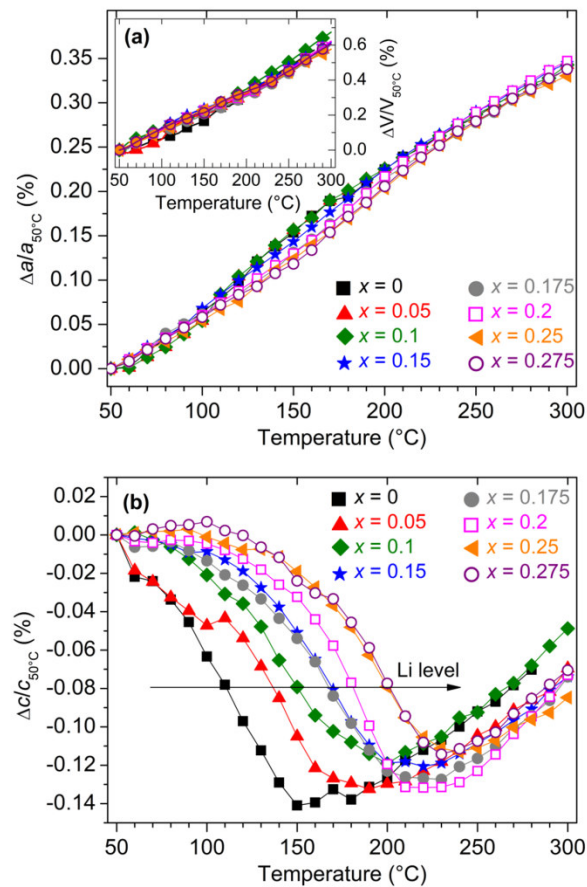


Fig. 11. Relative length change of cell parameters (a and c) and cell volume (inset) with temperature of $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ samples sintered at 1300 °C derived from powder XRD measurements. The relative change is related to the values at 50 °C. The uncertainties of the data are smaller than the symbol size.

As seen in Fig. 12 (see also Fig. S9, supporting information) the minimum of the lattice parameter c is near the maximum of the permittivity, indicating the polarization is along the c -axis. A corresponding thermal behavior of the cell parameters was reported for $\text{Sr}_y\text{Ba}_{1-y}\text{Nb}_2\text{O}_6$ with $y = 0.61$ and 0.82 [56,57]. Dilatometric measurements on single crystals of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ by Shorrocks et al. [58] reveal also a negative temperature coefficient for the lattice parameter c below the diffuse phase transition temperature. Moreover, our data show that the beginning of the shrinkage of the c -axis is shifted to higher temperatures with rising lithium content suggesting that the incorporation of lithium stabilizes the ferroelectric phase.

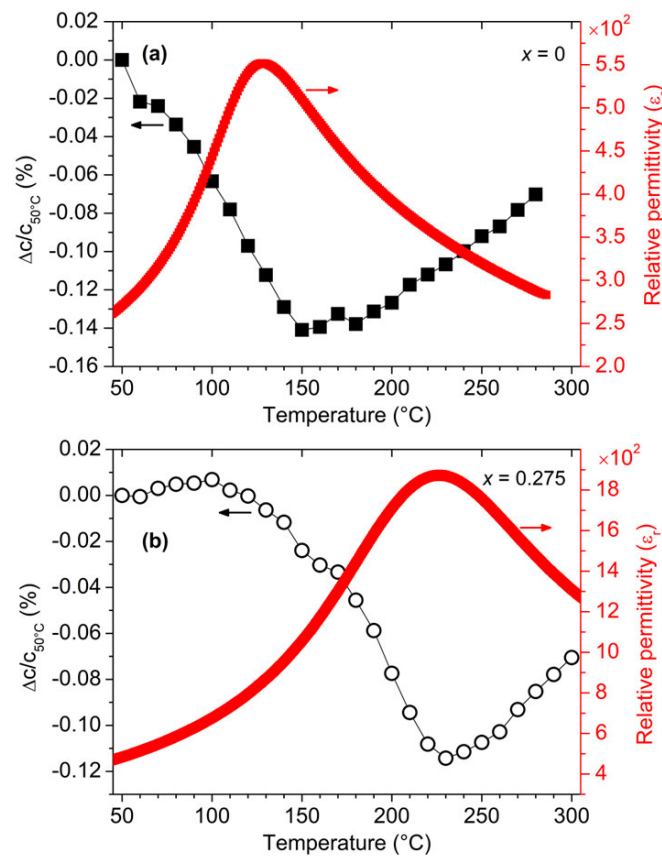


Fig. 12. Evolution of the *c*-axis (relative length change $\Delta c/c_{50^\circ\text{C}}$) and permittivity depending on temperature for $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics with $x = 0$ (a) and $x = 0.275$ (b). The relative length change $\Delta c/c_{50^\circ\text{C}}$ derived from powder XRD measurements is related to the value at 50 °C. The uncertainties of the data are smaller than the symbol size.

It is known that the ferroelectric $\rightleftharpoons$ paraelectric phase transition in displacive ferroelectric niobates is accompanied by the displacement of the niobium atoms [50]. Fig. 13 shows the shift of the *z*-coordinate of both crystallographic independent niobium atoms Nb(1) and Nb(2) with increasing temperature for the two samples with $x = 0$ and $x = 0.275$. The Nb(2) position (Wyckoff site: 8*d*) in both samples shows a gradually decreasing trend with rising temperature while the fractional coordinate of Nb(1) (Wyckoff site: 2*b*) increases only slightly, suggesting that the displacement of Nb(2) is mainly responsible for the ferroelectric (relaxor) behavior in accordance with PDF analysis by Pásciak et al. [8]. The *x*- and *y*-positions do not change

significantly with temperature (Fig. S10, supporting information). Similar results have been reported for $\text{Sr}_y\text{Ba}_{1-y}\text{Nb}_2\text{O}_6$ with $y = 0.33$ and 0.67 [59].

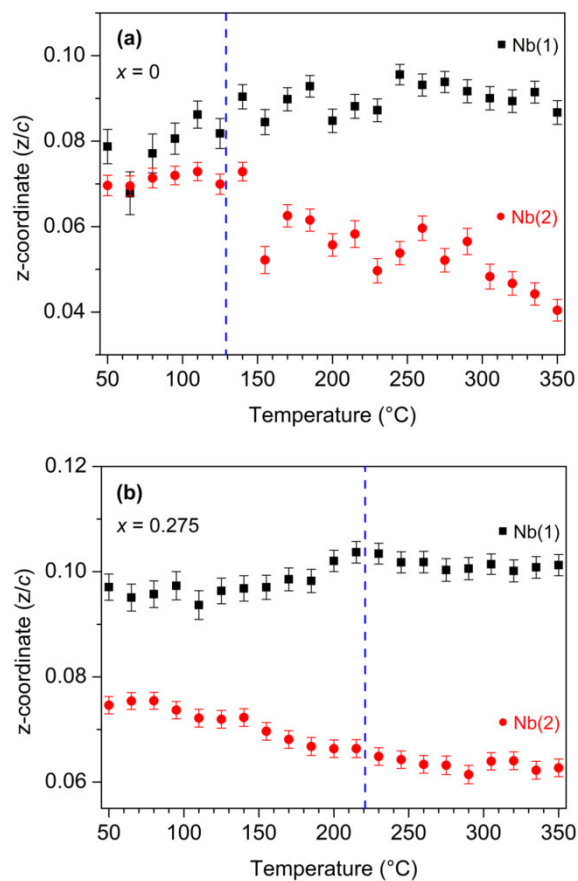


Fig. 13. Temperature-dependent shift of the fractional z-coordinate of both niobium sites in $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics with $x = 0$ (a) and $x = 0.275$ (b). The vertical blue dashed line represents the temperature of the permittivity maximum.

4. Conclusion

Ferroelectric $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics were prepared by conventional solid state synthesis. A solid solution is formed up to a lithium content of $x = 0.275$ whereas higher lithium levels lead to the formation of LiNbO_3 as secondary phase. The incorporation of lithium leads to an improved densification of ceramic bodies, rising grain sizes and the

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gradual formation of pillar-like grains, while leaving the optical band gap unaffected. Dielectric measurements reveal a relaxor behavior and the diffuseness of the ferroelectric $\rightleftharpoons$ paraelectric phase transition increases with x . The temperature of the permittivity maximum (T_m) shifts towards higher temperatures with higher lithium contents (x) indicating a stabilization of the ferroelectric phase at higher temperatures and enabling a tunability of T_m between 129–221 °C. The DC resistivity moderately increases with lithium incorporation, whereas higher lithium levels caused declining resistivity values. XRD investigations show a decrease of the cell parameter c in all samples with rising temperature. The length of the c -axis reaches a minimum near the phase transition region and then increases with temperature. In contrast, the cell parameter a continuously increases with temperature. The Nb(2) site shows a shift in the z -position with temperature, which is most likely linked with the ferroelectric behavior of $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$.

Appendix A. Supplementary data

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

Captions

Fig. 1

The tetragonal tungsten bronze structure of strontium barium niobate viewed along [001].

Fig. 2

Room temperature XRD patterns of $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics sintered at 1300 °C for 1 h. The inset shows a magnification of the pattern for $x = 0.3$.

Fig. 3

Evolution of the tetragonal lattice parameters of $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ depending on the lithium content (x) at room temperature. The uncertainties of the data are smaller than the symbol size.

Fig. 4

Relative bulk densities of ceramic bodies in dependence of x after sintering at 1300 °C for 1 h (heating-/cooling rate 5 K min⁻¹). The inset shows the absolute bulk densities. The uncertainties of the data in the inset are smaller than the symbol size.

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Fig. 5

SEM-BSE images of selected $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramic bodies sintered at 1300 °C for 1 h. a) $x = 0$, b) $x = 0.1$, c) $x = 0.2$, d) $x = 0.275$. The inset in (d) shows a very large irregular grain.

Fig. 6

Optical band gap energies (indirect allowed) of $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics sintered at 1300 °C for 1 h. The inset exemplarily shows $(F(R) \cdot h\nu)^{1/2}$ versus $h\nu$ for a ceramic sample with $x = 0.2$.

Fig. 7

Temperature dependence of the relative permittivity (ϵ_r) and dissipation factor ($\tan \delta$) at 1 MHz for $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics sintered at 1300 °C.

Fig. 8

Evolution of the temperature of the permittivity maximum (T_m) depending on the composition x at 1 MHz. The inset shows the permittivity values depending on x at T_m (a) and at room temperature (b).

Fig. 9

Diffuseness coefficient versus lithium content (x) for ceramic samples sintered at 1300 °C.

Fig. 10

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Development of the specific DC resistivity with lithium content (x) of $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics.

Fig. 11

Relative length change of cell parameters (a and c) and cell volume (inset) with temperature of $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ samples sintered at 1300 °C derived from powder XRD measurements. The relative change is related to the values at 50 °C. The uncertainties of the data are smaller than the symbol size.

Fig. 12

Evolution of the c -axis (relative length change $\Delta c/c_{50^\circ\text{C}}$) and permittivity depending on temperature for $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics with $x = 0$ (a) and $x = 0.275$ (b). The relative length change $\Delta c/c_{50^\circ\text{C}}$ derived from powder XRD measurements is related to the value at 50 °C. The uncertainties of the data are smaller than the symbol size.

Fig. 13

Temperature dependent shift of the fractional z -coordinate of both niobium sites with temperature in $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics with $x = 0$ (a) and $x = 0.275$ (b). The vertical blue dashed line represents the temperature of the permittivity maximum.

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Supporting Information

Impact of Li-substitution on dielectric, structural and sintering behavior of

$\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics

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Tab. S1: Theoretical bulk densities of $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$

$\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$	Calculated theoretical bulk densities* of the ceramics according to [1,2] (g cm^{-3})
$x = 0$	5.37
$x = 0.05$	5.35
$x = 0.10$	5.34
$x = 0.15$	5.32
$x = 0.175$	5.31
$x = 0.20$	5.30
$x = 0.25$	5.29
$x = 0.275$	5.28

* The theoretical bulk densities represent the maximum achievable densities.

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Tab. S2: Grain sizes of ceramics

$\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$	Grain size (μm)
$x = 0$	irregular-/globular: 1.5–14* ($\bar{\phi}_{\text{li}} = 6.7(3)$)
$x = 0.05$	irregular-/globular: 1.6–14 ($\bar{\phi}_{\text{li}} = 7.1(4)$)
$x = 0.1$	irregular-/globular: 2.0–17 ($\bar{\phi}_{\text{li}} = 8.5(5)$)
$x = 0.15$	irregular-/globular: 2.2–26 ($\bar{\phi}_{\text{li}} = 10(1)$) pillars: 4–8 _W × 6–16 _L
$x = 0.175$	irregular-/globular: 2.0–23 ($\bar{\phi}_{\text{li}} = 10(1)$) pillars: 4–10 _W × 6–27 _L
$x = 0.2$	irregular-/globular: 1.8–27 ($\bar{\phi}_{\text{li}} = 12(1)$) pillars: 4–11 _W × 5–25 _L
$x = 0.25$	irregular-/globular: 4–83 ($\bar{\phi}_{\text{li}} = 16(3)$) pillars: 4–14 _W × 5–50 _L
$x = 0.275$	no irregular-/globular grains pillars: 3–25 _W × 5–74 _L , large crystals up to 50 _W × 125 _L

$\bar{\phi}_{\text{li}}$: average grain size of the irregular-/globular shaped grains estimated by the lineal intercept method [1].

* The range represents the smallest and largest grains.

L: length; W: width

The fraction of the pillar-like grains increases with x .

- [1] M. I. Mendelson, J. Am. Ceram. Soc. 52 (1969) 443.

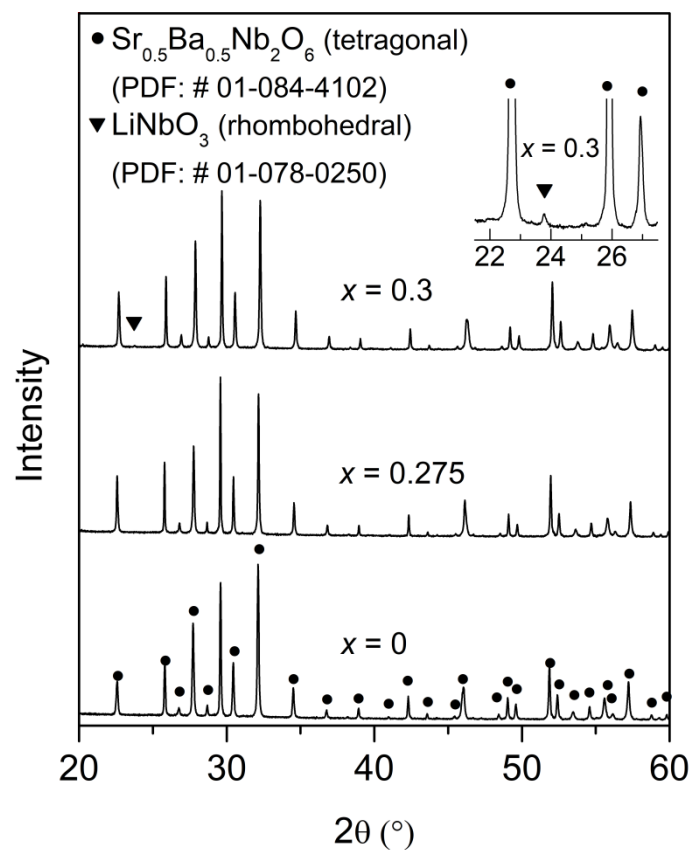


Fig. S1: Room temperature XRD patterns of selected $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ preceramic powders calcined between 1200–1250 °C. The inset shows a magnification of the pattern for $x = 0.3$ recorded with a prolonged counting time.

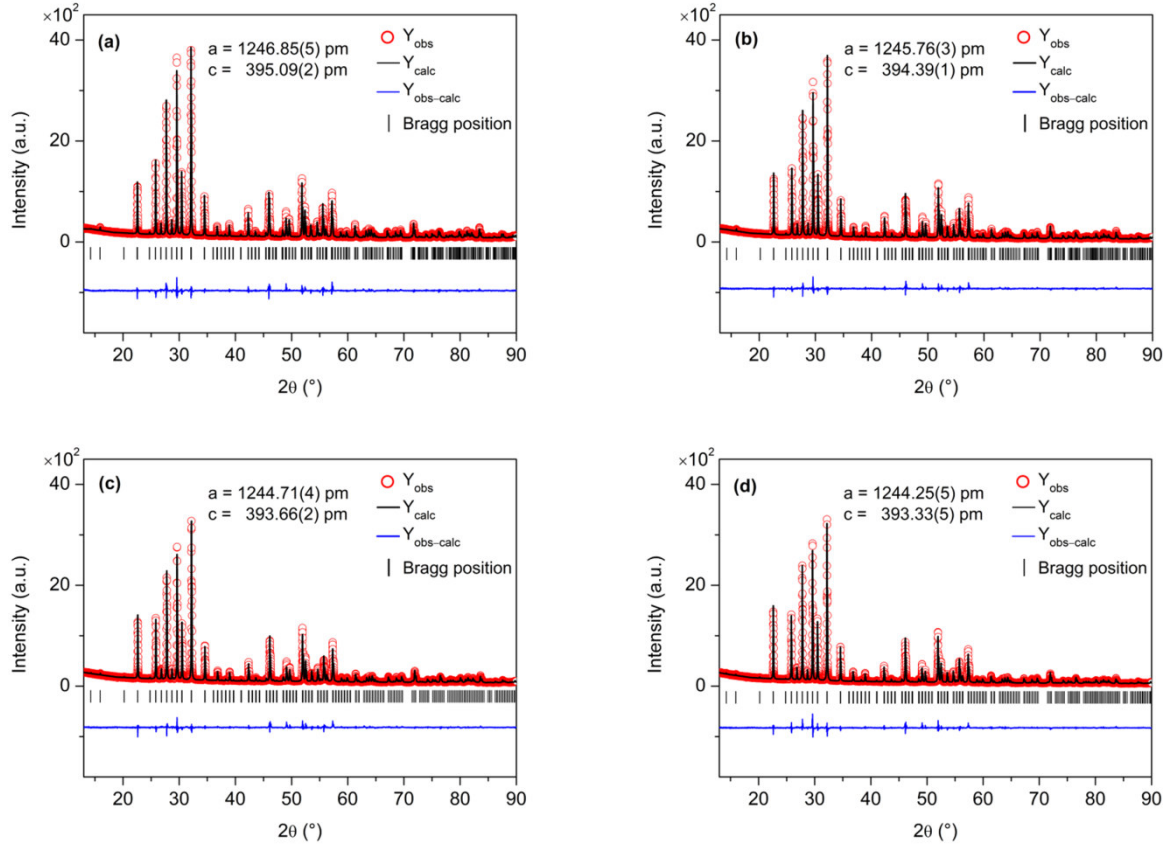


Fig. S2: Rietveld refinements (Cu-K $_{\alpha 1+\alpha 2}$ radiation) of selected $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics sintered at 1300 °C for 1 h. a) $x = 0$ ($R_p = 4.16\%$, $R_{wp} = 5.55\%$, $\chi^2 = 4.53$), b) $x = 0.1$ ($R_p = 3.82\%$, $R_{wp} = 5.02\%$, $\chi^2 = 3.09$), c) $x = 0.2$ ($R_p = 3.74\%$, $R_{wp} = 4.96\%$, $\chi^2 = 3.23$), d) $x = 0.275$ ($R_p = 3.98\%$, $R_{wp} = 5.28\%$, $\chi^2 = 3.10$).

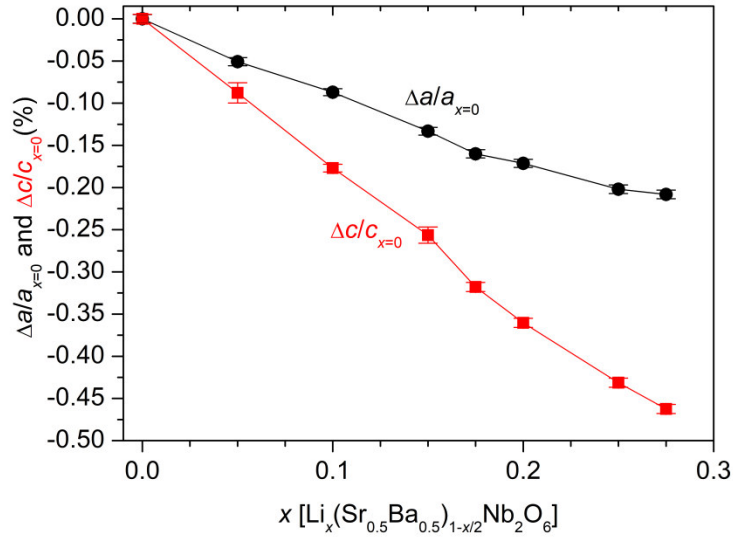


Fig. S3: Relative length changes of the tetragonal lattice parameters depending on the lithium content (x) for $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics sintered at 1300 °C for 1 h. The relative length change is related to the lattice parameters for the sample with $x = 0$.

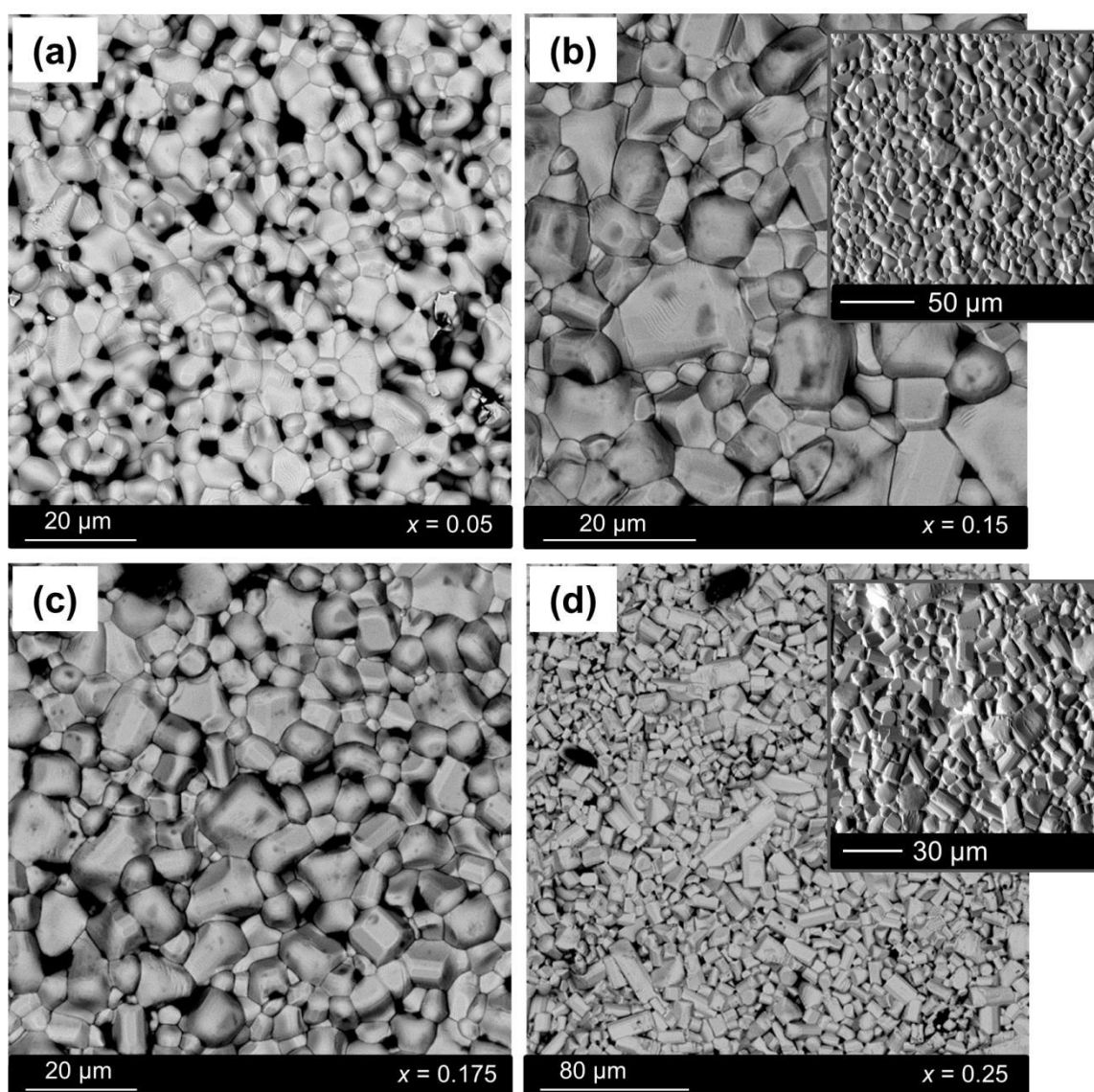


Fig. S4: SEM-BSE images of selected $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramic bodies sintered at 1300 °C for 1 h. a) $x = 0.05$, b) $x = 0.15$, c) $x = 0.175$, d) $x = 0.25$. The insets in b) and d) shows the microstructure recorded in a topographical mode.

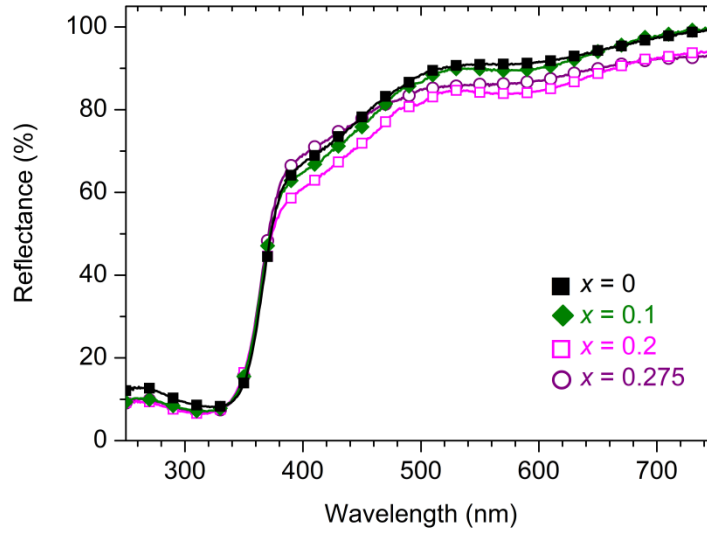


Fig. S5: Diffuse reflectance spectra of selected powdered $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics sintered at 1300 °C for 1 h. For the sake of clarity only selected spectra are shown and every 20th data point is represented by a symbol.

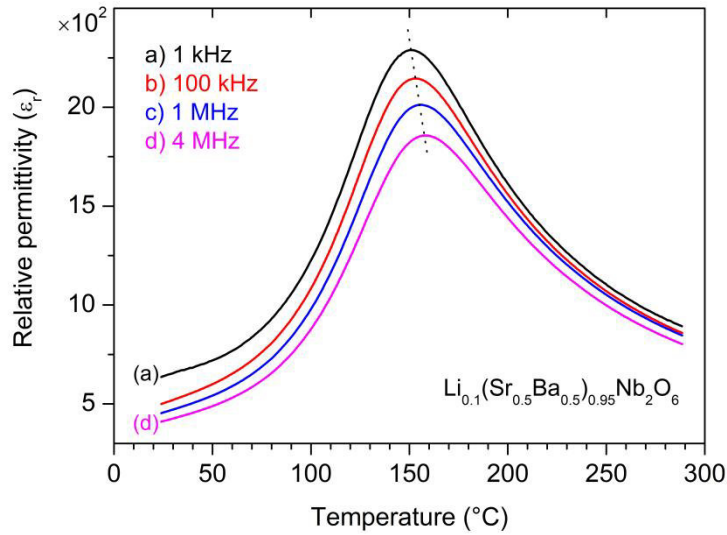


Fig. S6: Temperature dependence of ϵ_r at different frequencies demonstrated for $\text{Li}_{0.1}(\text{Sr}_{0.5}\text{Ba}_{0.5})_{0.95}\text{Nb}_2\text{O}_6$ ceramics sintered at 1300 °C for 1 h.

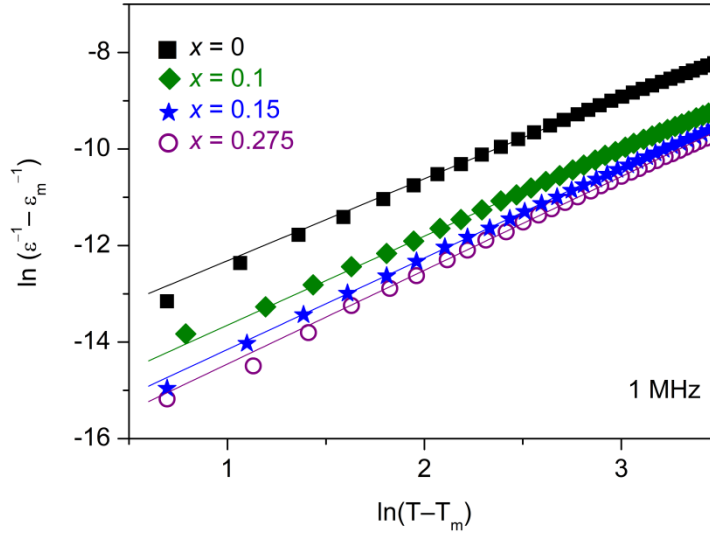


Fig. S7: Plot of $\ln(\epsilon^{-1} - \epsilon_m^{-1})$ as a function of $\ln(T - T_m)$ for selected $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics sintered at 1300 °C for 1 h. Lines are the fit results, while symbols correspond to experimental data.

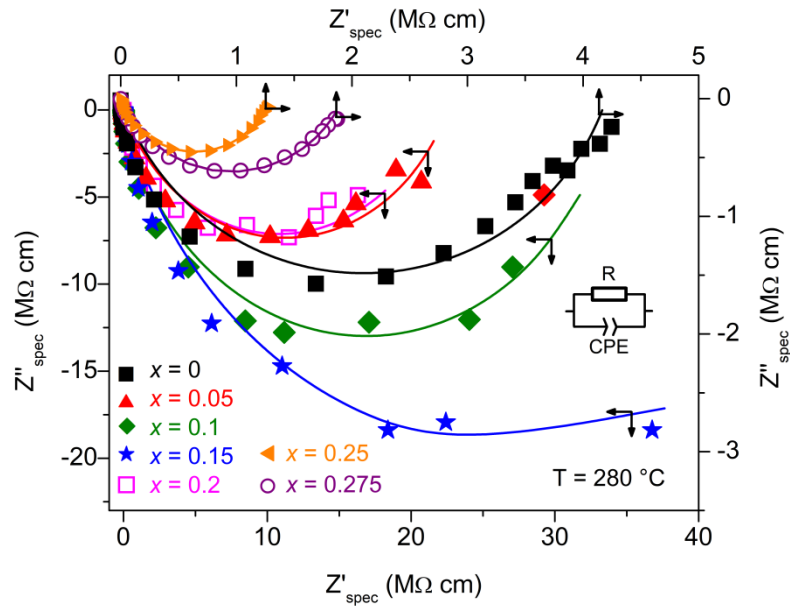


Fig. S8: Cole-Cole plots measured at the indicated temperature for $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics sintered at 1300 °C for 1 h. Fits were carried out using the shown equivalent circuit. Lines are the fit results, while symbols correspond to experimental data. Errors bars are omitted for clarity. The uncertainties of the experimental data are between 5–10 %.

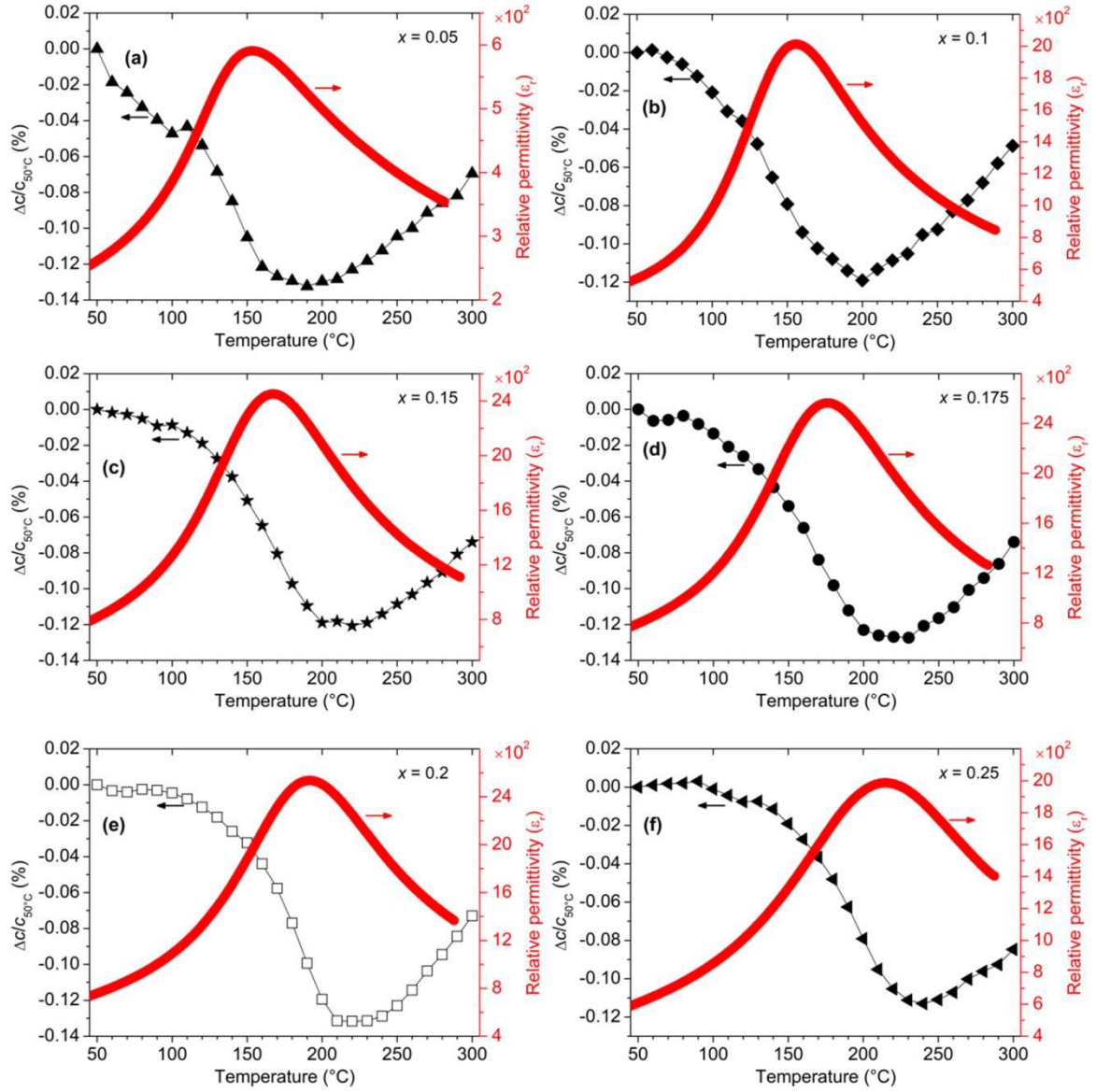


Fig. S9: Relative length change of the c -axis together with the development of the permittivity depending on temperature for $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics, sintered at 1300°C with $x = 0.05$ (a), $x = 0.1$ (b), $x = 0.15$ (c), $x = 0.175$ (d), $x = 0.2$ (e), and $x = 0.25$ (f). The relative length change $\Delta c/c_{50^\circ\text{C}}$ is related to the value at 50°C . The uncertainties of the data are smaller than the symbol sizes.

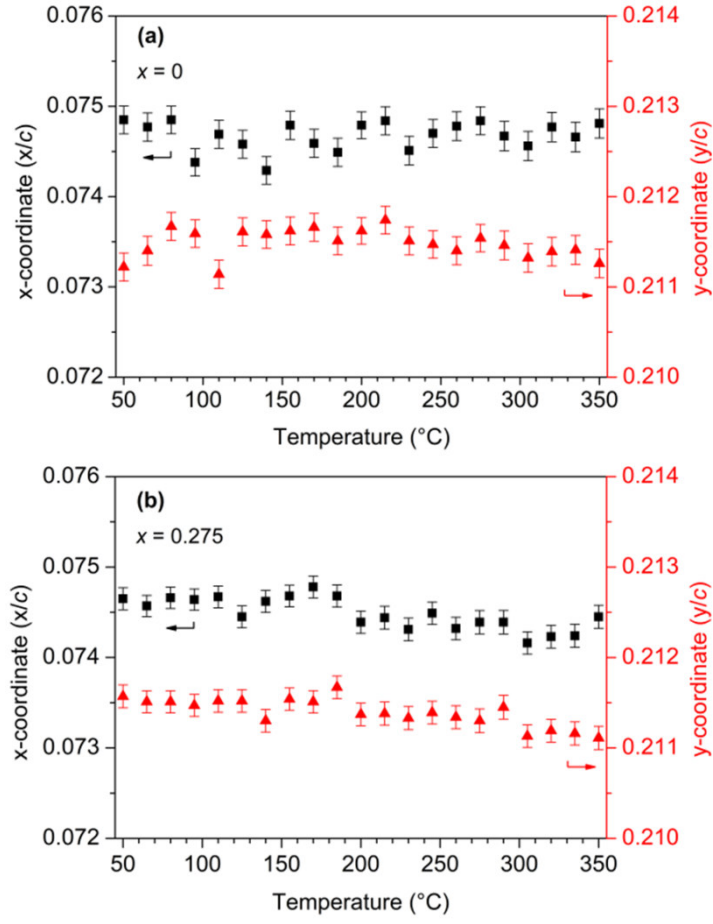


Fig. S10: Shift of the fractional x- and y-coordinates of the Nb(2) site (Wyckoff site: 8d) with temperature for $\text{Li}_x(\text{Sr}_{0.5}\text{Ba}_{0.5})_{1-x/2}\text{Nb}_2\text{O}_6$ ceramics with $x = 0$ (a) and $x = 0.275$ (b).