Remarkable Strontium *B*-Site Occupancy in Ferroelectric Pb(Zr$_{1-x}$Ti$_x$)O$_3$

Solid Solutions Doped with Cryolite-Type Strontium Niobate

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Abstract

New high-performance ferroelectric materials based on Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (*PZT*) that are doped with cryolite-type strontium niobate (*SNO*, Sr$_4$(Sr$_{2-2y/3}$Nb$_{2+2y/3}$)O$_{11+y}$V$_{O,1-y}$ with $0{\leq}y{\leq}1$), hence denoted *PZT:SNO*, and their microscopic structure are described. The combination of exceptional piezoelectric properties, i.e. a piezoelectric strain constant of $d_{33}{\approx}760$ pm/V, with excellent stability and degradation resistance makes ferroelectric *PZT:SNO* solid solutions very attractive for use in novel and innovative piezoelectric actuator and transducer applications. Extended X-ray absorption fine-structure (EXAFS) analyses of *PZT:SNO* samples revealed that ~10 % of the Sr cations occupy the nominal *B*-sites of the perovskite-type *PZT* host lattice. This result was supported by EXAFS analyses of both a canonical SrTiO$_3$ perovskite and two *SNO* model and reference compounds. Fit models that do not account for Sr cations on *B*-sites were ruled out. A clear Sr-Pb peak in Fourier transformed EXAFS data visually confirmed this structural model. The generation of temporary oxygen vacancies and the intricate defect chemistry induced by *SNO*-doping of *PZT* are crucial for the exceptional materials properties exhibited by *PZT:SNO* materials.

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I. Introduction

Ferroelectric ceramic perovskites with ABO$_3$-type structure such as lead zirconium titanium oxide Pb(Zr,Ti)O$_3$ and its solid solutions represent the most widely used class of materials in piezoelectric actuators and transducers for their piezoelectric and dielectric properties.[1,2] Among this class of materials, Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (*PZT*) solid solutions have attracted great attention. They are ferroelectric over a wide composition range and exhibit a high Curie temperature.[1] The phase diagram of Pb(Zr$_{1-x}$Ti$_x$)O$_3$ is characterized by an unusual, nearly temperature independent morphotropic phase boundary (MPB) around $x \approx 0.45$-0.50 that separates regions with rhombohedral and tetragonal ferroelectric crystal structure.[1] In addition, Pb(Zr$_{1-x}$Ti$_x$)O$_3$ with $x \approx 0.45$-0.50 features a monoclinic bridging phase between tetragonal and rhombohedral regions.[3] As a result, Pb(Zr$_{1-x}$Ti$_x$)O$_3$ solid solutions with compositions near the MPB exhibit unusually large piezoelectric coefficients and electromechanical responses.[1,2,4,5]

The piezoelectric properties of *PZT* can change favorably in response to solid solution formation with certain compounds or doping agents, offering the possibility to tailor its properties for new applications.[1,2] In conjunction with relatively low production costs, the unique piezoelectric, electromechanical, and dielectric properties make *PZT* and its solid solutions the material of choice for many commercial and industrial piezoelectric applications.[2,5-7] Recently, innovative piezoelectric multilayer actuator-based diesel and gasoline injection systems were developed by major automotive suppliers (i.e. Bosch, Denso, Delphi, SiemensVDO, Toyota, etc.); and in the meantime they have already found widespread application in automotive industry.[5,8-11] Owing to the fast electromechanical response time and the high blocking force of *PZT*-based piezoelectric multilayer actuators used in these innovative applications, the fuel injection valves can be operated at least four times faster compared to conventional solenoid-based fuel injection systems, thus enabling at least five separate fuel

injections during one fuel injection cycle.[5,8-11] Improved fuel economy, reduced exhaust and noise emissions, and enhanced engine performance are striking benefits directly associated with this new piezoelectric actuator-based fuel injection technology.

Aside from plain product performance, aspects like product quality and reliability as well as temporal and thermal stability are fundamentally important for high-performance electronic products. Special ferroelectric solid solution materials have therefore been developed and prepared from Pb(Zr$_{1-x}$Ti$_x$)O$_3$ ($x\approx$0.45-0.50) with specific doping agents so as to optimize performance, reliability, degradation stability, and quality of piezoelectric ceramics for use in piezoelectric actuator applications.[12-22]

As part of our continuing program to develop new high-performance ferroelectric materials, we recently developed and described novel perovskite-type Pb(Zr$_{1-x}$Ti$_x$)O$_3$ solid solutions that are doped with cryolite-type strontium niobate (*SNO*) according to the general formula *SNO* = Sr$_4$(Sr$_{2-2y/3}$Nb$_{2+2y/3}$)O$_{11+y}$V$_{O,1-y}$ (0$\leq y\leq$1; V_O: oxygen vacancy).[23,24] *SNO*-doped *PZT* materials, denoted *PZT:SNO*, exhibit exceptional piezoelectric properties and have been used successfully to manufacture high-performance piezoelectric multilayer actuators. Owing to their large piezoelectric strain constant of $d_{33}\approx$760 pm/V (measured at an electric field of E=2 kV/mm), respective piezoelectric multilayer actuators exhibit unusually large electromechanical strains of $S\approx$0.15-0.16 %, where $S=\Delta L/L$ and L represents the length of the multilayer actuator. The unique combination of a high piezoelectric strain constant with the excellent materials stability and the high Curie temperature is caused by doping of *PZT* with cryolite-type *SNO* and by microstructure optimization in *PZT:SNO* materials.[23,24]

We performed extended X-ray absorption fine-structure (EXAFS) analyses to gain a better microscopic understanding of these new piezoelectric *PZT:SNO* solid solutions,

particularly targeting the strontium ion (Sr^{2+}) coordination environment and crystal lattice site occupancy in ferroelectric perovskite-type *PZT:SNO* materials as well as in SrTiO$_3$ and different *SNO* model and reference compounds.

In this paper, we report and discuss the results of our EXAFS analysis of *PZT:SNO* high-performance piezoelectric materials. In addition, we discuss their underlying intricate defect chemistry that is central to their exceptional materials properties.

II. Experimental Section

Preparation of Ceramic Samples: The ceramic samples were prepared by mixed-oxide synthesis routes. Sample preparation was carried our by wet-chemical mixing of appropriate amounts of commercially available, high-quality raw materials such as Pb$_3$O$_4$, ZrO$_2$, TiO$_2$, SrCO$_3$, and Nb$_2$O$_5$ with sufficiently small grain size (d$_{50}$≤1 µm). After sample isolation and drying, the corresponding powder mixtures were calcined in air, followed by wet-chemical ball-mill treatment with ZrO$_2$ grinding media to yield a grain size of d$_{50}$≈0.4-0.5 µm. Wet-chemical sample treatment in alcohol turned out to be advantageous. The dried powder samples were then converted into pressed-pellet samples and sintered in air to afford sintered-pellet samples with a relative density of ρ_{rel}~95 %.

SrTiO$_3$ Model Compounds: Samples of the perovskite-type model compound SrTiO$_3$ (*STO*) were prepared from SrCO$_3$ and TiO$_2$. After calcination at 1150 °C for 6 h and subsequent fine-milling, the pressed-pellet samples were sintered at 1250 °C for 4 h.

SNO **Dopants and Model Compounds**:   Samples of cryolite-type strontium niobate Sr$_4$(Sr$_{5/3}$Nb$_{7/3}$)O$_{11.5}$$V_{O;0.5}$ (*SNO-1*; V_O: oxygen vacancy) and Sr$_4$(Sr$_{4/3}$Nb$_{8/3}$)O$_{12}$ (*SNO-2*) were prepared analogously from SrCO$_3$ and Nb$_2$O$_5$. To promote the formation of their more complicated cryolite-type structure, the *SNO* samples were subjected to a two-fold calcination treatment. The first calcination at 1100 °C for 4 h was followed by ball-mill treatment for about 0.5 h. The isolated and dried powder mixtures were then subjected to a second calcination treatment at 1250 °C for 4 h, followed by a second ball-mill treatment. Respective pressed-pellet samples were sintered in air at 1400 °C for 4 h.

Ferroelectric *PZT:SNO* Ceramics:

a. *Precursor Mixed-Oxide Route*:   *PZT:SNO* solid solution samples (*PZT* doped with cryolite-type strontium niobate, *SNO*) were prepared with a small excess of PbO as sintering aid material,

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for example with a composition according to formula *PZT:SNO-1* = (*PZT*)$_{0.995}$(*SNO-1*)$_{0.005}$(PbO)$_{0.01}$. Pb(Zr$_{0.52-0.53}$Ti$_{0.48-0.47}$)O$_3$ (*PZT*) and cryolite-type doping agent *SNO* were prepared separately by mixing appropriate amounts of raw materials Pb$_3$O$_4$, ZrO$_2$, and TiO$_2$ for *PZT*, and SrCO$_3$ and Nb$_2$O$_5$ for *SNO-1* and *SNO-2*. The *PZT* precursor powder was calcined in air at 925 °C for 6 h, and the *SNO* precursor powders were calcined twice as described above. After calcination, the *PZT* and *SNO* precursor powders were thoroughly mixed, followed by ball-mill treatment and subsequent formation of pressed-pellet samples. Sintering in air at 1100 °C for 4 h afforded sintered-pellet samples of *PZT:SNO* with a relative density of ρ_{rel}≈95 %.

b. *Conventional Mixed-Oxide Route*: Alternatively, *PZT:SNO* samples were prepared by mixing appropriate amounts of raw materials Pb$_3$O$_4$, ZrO$_2$, TiO$_2$, SrCO$_3$, and Nb$_2$O$_5$. After thorough mixing of the raw materials, ball-milling, calcination in air at 925 °C for 6 h, ball-milling, and sintering in air at 1100 °C for 4 h, sintered-pellet samples of *PZT:SNO* prepared by this synthesis route exhibited indistinguishable XRD patterns and materials properties when compared to respective *PZT:SNO* samples prepared by the *Precursor Mixed-Oxide Route*.

Particle Size Analysis: Average grain sizes and grain size distributions of powder samples were measured by light scattering of diluted aqueous or alcoholic dispersions using a MALVERN 2000 Mastersizer.

Sample Density Measurements: The experimental sample density (ρ_{exp}) of sintered-pellet samples was determined (i) by precision weighing and measuring of geometric dimensions of 10 sintered pellets per sample, and (ii) by the *Archimedes* method. The results of both experimental density determination methods were very similar. The theoretical sample density (ρ_{theo}) was derived from X-ray diffraction (XRD) analysis. The relative sample density (ρ_{rel}) was calculated according to $\rho_{rel}=\rho_{exp}/\rho_{theo}$.

X-Ray Diffraction (XRD) Analysis: Powderized sintered-pellets of samples *SNO-1*, *SNO-2*, *STO*, and *PZT:SNO* were characterized by X-ray diffraction (XRD) analysis using a Bruker AXS (Karlsruhe, Germany) D5005 θ/θ diffractometer with Cu-K_α radiation. The diffractometer was equipped with an automatic divergence slit system, a rotating sample holder (30 rpm), a secondary graphite monochromator, and a scintillation counter. The samples were analyzed in the range of 2θ=20–60° (*STO* samples) and 2θ=5–130° (*PZT*, *PZT:SNO*, and *SNO* samples) using a step width of 0.02° and a constant counting time of 10 sec per step. Refinement of lattice constants and crystal structure according to the Rietveld profile fitting method was performed with the *TOPAS* software package (Bruker AXS, Karlsruhe, Germany). During Rietveld analysis, sample displacement and six background parameters, fitted using a polynomial of 6th degree, were refined as general parameters. For each crystal phase, the scale factor and lattice constants, the pseudo-*Voigt* peak profile coefficients, the atomic parameters, and the occupancy and thermal parameters were calculated in subsequent refinement cycles.

Extended X-ray absorption fine-structure (EXAFS) Analysis: Sintered pressed-pellet samples were ground under acetone, passed through a 32 μm sieve, brushed onto adhesive tape, and stacked such that the change in the absorption corresponded to about half of an absorption length at the Sr *K*-edge (16105 eV) for *SNO-1*, *SNO-2*, *STO*; considerably less for *PZT:SNO*. EXAFS measurements were performed on beamline *10-2* at the Stanford Synchrotron Radiation Laboratory (*SSRL*) after loading the samples in a liquid He flow-cryostat and positioning the samples at an angle of 50° with respect to the X-ray beam. All EXAFS data were collected both in transmission and fluorescence mode with a 30-element Ge fluorescence detector, although only the fluorescence data were usable for *PZT:SNO*. Data were acquired at the Sr *K*-edge in the temperature range of 20-300 K. The Si (220) monochromator was detuned by 75 % to reduce harmonic contamination. High quality EXAFS data were obtained for all samples. Typically

two to three scans were performed on samples of model compounds *STO*, *SNO-1* and *SNO-2*, but

17 scans were run on *PZT:SNO* samples over the course of about 7.5 hours.

The EXAFS function $\chi(k)$ describes the normalized oscillations measured above a given

absorption edge.[25] The photoelectron wave vector k is determined by

$k = \sqrt{(8\pi^2 m_e / h^2)(E - E_0)^2}$, where m_e is the electron rest mass and E is the photon incident

energy. E_0 is the photoelectron threshold energy, arbitrarily determined from the energy position

of the half-height of the given absorption edge. The outgoing photoelectron can be backscattered

by neighboring atoms and can therefore interfere with itself in the vicinity of the absorbing atom.

This interference modulates the absorption coefficient in a manner proportional to the number of

generated photoelectrons. χ is therefore defined as $\chi = \mu_a/\mu_0 - 1$, where μ_a is the absorption from

the atomic species of interest and μ_0 is an approximation of this absorption in the absence of

EXAFS oscillations. In fluorescence mode EXAFS measurements, the true χ is approximated by

$\chi_{exp} = I_f/I_0 - 1$, where I_f is the measured fluorescence flux and I_0 is the incident flux. As these data

are subject to self-absorption of the fluorescence photons, we made a correction for this effect to

obtain an approximation to the true χ.[26] Given the high quality of the transmission data on *STO*

samples, we were able to verify the accuracy of the self-absorption correction on the

fluorescence data. Although the correction was quite large (20-30 %) in the model compounds,

the correction was only about 1 % in case of *PZT:SNO* samples where only the fluorescence data

is usable. The data were also corrected for the dead time of the Ge detector. All recorded

EXAFS data were reduced and fit in real space using the *RSXAP* programs,[27-29] utilizing

theoretical photoelectron backscattering amplitudes and phases generated by the *FEFF7* code.[30]

In particular, μ_0 was approximated by a 7-knot cubic spline.

III. Results and Discussion

X-Ray Diffraction (XRD) Analysis: The results of our X-ray crystallography and XRD analysis of *STO* samples confirmed the well known perovskite-type structure of SrTiO$_3$ with a=3.90489(1) Å. In the ideal perovskite ABO$_3$ lattice with a cubic unit cell as shown in Figure 1, Sr^{2+} ions on *A*-sites are surrounded by the faces of [TiO$_{6/2}$]$^{2-}$ octahedra. Sr^{2+} ions on *A*-sites therefore possess 12 immediate oxygen neighbors, so-called Sr(*A*)-O neighbors, at a distance of R≈2.76 Å.

Figure 2 shows a representative XRD pattern of *PZT:SNO-1* = [(*PZT*)$_{0.995}$(*SNO-1*)$_{0.005}$ (PbO)$_{0.01}$]. The unit cell is closely related to the ideal perovskite structure shown in Figure 1. However, the structure of *PZT:SNO-1* is modified from the ideal ABO$_3$ structure by ferroelectric tetragonal and rhombohedral distortions that result from the specific Zr^{4+}-to-Ti^{4+} ratio in *PZT* near the morphotropic phase boundary (MPB), that is for x≈0.45-0.50 in Pb(Zr$_{1-x}$Ti$_x$)O$_3$.[1] In our case, parameter x was fixed to 0.47≤x≤0.48. The XRD patterns show no indications for secondary phases such as PbO or Pb$_2$Nb$_2$O$_7$ (pyrochlore). The individual contributions and fractions of respective co-existing ferroelectric tetragonally and rhombohedrally distorted phases in *PZT:SNO* near the MPB were determined by Rietveld refinement calculations. For *PZT:SNO-1*, the fractional contribution of the tetragonal phase is 48.9 mass-% with lattice constants of a=4.0440(7) Å and c=4.1238(8) Å, while the fraction of the rhombohedral phase is 51.1 mass-% with lattice constants of a=5.768(6) Å and c=7.06(1) Å. These values are controlled by parameter x according to general formula Pb(Zr$_{1-x}$Ti$_x$)O$_3$.[1] As expected, the small excess of about 1 mol-% of PbO that was added as sintering aid material, and the low concentration (≈0.5 mol-%) of cryolite-type dopant *SNO-1* = Sr$_4$(Sr$_{5/3}$Nb$_{7/3}$)O$_{11.5}$$V_{O;0.5}$, which forms a solid solution with the *PZT* host lattice, could not be detected by XRD analysis.

The cryolite-type structure of dopant *SNO-1*, illustrated schematically in Figure 3a, is closely related to the perovskite-type *AB*O$_3$ structure (Figure 1). This relation becomes readily apparent by comparison with Figure 3b, which shows a portion of the upper right region of the unit cell displayed in Figure 3a. With the co-existence of both Sr^{2+} and Nb^{5+} ions, octahedral *B*-sites in the cryolite-type structure of *SNO-1* (Figure 3a) are predominantly occupied by Sr^{2+} and Nb^{5+} ions in alternating sequence. This leads to a doubling of the lattice parameter, and therefore an enlarged unit cell containing two formula units of *SNO-1* according to Sr$_8$(Sr$_{10/3}$Nb$_{14/3}$)O$_{23}$$V_{O;1}$ = 2 × Sr$_4$(Sr$_{5/3}$Nb$_{7/3}$)O$_{11.5}$$V_{O;0.5}$ is obtained. Based on the face-centered cubic (fcc) packing of [SrO$_3$]$^{4-}$ units, the [NbO$_{6/2}$]$^-$ octahedra are slightly contracted owing to higher charged Nb^{5+} ions ($r_{Nb(5+),CN=6}$=0.64 Å). The contraction of the [NbO$_{6/2}$]$^-$ octahedra makes it possible for larger Sr^{2+} ions ($r_{Sr(2+), CN=6}$=1.18 Å) to occupy the center position (*B*-site) of adjacent [SrO$_{6/2}$]$^{4-}$ octahedra (Figure 3a).

A representative XRD pattern of cryolite-type dopant Sr$_4$(Sr$_{5/3}$Nb$_{7/3}$)O$_{11.5}$$V_{O;0.5}$ (*SNO-1*) is depicted in Figure 4. Rietveld refinement confirmed the cryolite-type structure of *SNO-1*. The space group *F*m3m with *a*=8.29833(3) Å was determined, not only based on the assumption of ideal crystallographic positions in the cryolite-type structure for *SNO-1*, but also when split positions (i) of Sr^{2+} and (ii) of Sr^{2+} and O^{-II} were used for Rietveld refinement. The XRD data are in good agreement with previous studies[31,32] of the SrO-Nb$_2$O$_5$ phase diagram that revealed the existence of a non-stoichiometric region corresponding to general *SNO* formula Sr$_4$(Sr$_{2-2y/3}$Nb$_{2+2y/3}$)O$_{11+y}$$V_{O;1-y}$ (0≤*y*≤1). While for a compound with the composition Sr$_4$(Sr$_{1.44}$Nb$_{2.56}$)O$_{11.84}$$V_{O;0.16}$ a cubic unit cell with *a*=8.277 Å was determined, XRD analysis of a material corresponding to formula Sr$_4$(Sr$_{1.92}$Nb$_{2.08}$)O$_{11.12}$$V_{O;0.88}$ resulted in a cubic unit cell with *a*=8.314 Å.[31] A strong correlation exists between the oxygen vacancy concentration [V_O] and the Sr^{2+}-to-Nb^{5+} ratio (B_{Sr}/B_{Nb}) on the octahedral *B*-sites in the material's crystal lattice.[31]

For the first boundary case with a material composition corresponding to formula Sr$_4$(Sr$_2$Nb$_2$)O$_{11}V_{O;1}$ (B_{Sr}/B_{Nb}=1 and y=0), a tetragonal lattice distortion with a=8.417 Å and c=16.41 Å was determined by XRD analysis and Rietveld refinement.[31] In this case, the enlarged unit cell comprised four formula units corresponding to Sr$_{16}$(Sr$_8$Nb$_8$)O$_{44}V_{O;4}$ = 4 × Sr$_4$(Sr$_2$Nb$_2$)O$_{11}V_{O;1}$, which includes four oxygen vacancies V_O.[31] For the second boundary case corresponding to the oxygen vacancy-free composition Sr$_4$(Sr$_{4/3}$Nb$_{8/3}$)O$_{12}$ = 4 × Sr(Sr$_{1/3}$Nb$_{2/3}$)O$_3$ = 4/3 × Sr$_4$Nb$_2$O$_9$ (*SNO-2*; B_{Sr}/B_{Nb}=1/2 and y=1), our XRD analysis and Rietveld refinement gave rise to a cubic unit cell with space group *Fm*3*m* and lattice parameter a=8.2671 Å. This lattice constant is in good agreement with the cubic *F*-centered unit cell with lattice parameter a=8.268(2) Å that was described previously[33,34] for a so-called high temperature (*HT*) modification of compound Sr$_4$Nb$_2$O$_9$ (*HT*-Sr$_4$Nb$_2$O$_9$) corresponding to the cryolite-type composition Sr[(Sr$_{2/3}$Nb$_{1/3}$)$_{1/2}$Nb$_{1/2}$]O$_3$ = 1/3 × Sr$_4$Nb$_2$O$_9$, featuring a 1:1 ordering of (Sr$_{2/3}$Nb$_{1/3}$):(Nb) on the nominal *B*-sites.[33,34] XRD and neutron scattering data indicated Sr(*A*-site)-O bond lengths in the range of R≈2.361-3.487 Å, and a Sr(*B*-site)-O bond length of R≈2.198 Å.[34] After annealing *HT*-Sr$_4$Nb$_2$O$_9$ samples at 1100-1200°C, a phase transition occurred and a low temperature (*LT*) polymorph phase (*LT*-Sr$_4$Nb$_2$O$_9$) was identified.[34] Transmission electron microscopy (TEM) analysis revealed that, in contrast to the *HT*-Sr$_4$Nb$_2$O$_9$ phase, the *LT*-Sr$_4$Nb$_2$O$_9$ polymorph with orthorhombic unit cell does not exhibit alternation of Nb- and Sr/Nb-occupied {111}$_c$ cation planes.[34] For *LT*-Sr$_4$Nb$_2$O$_9$, TEM data suggested a sequence of nine {111}$_c$ cation planes according to (Sr$_{1/2}$NbNbNbSrSrNbNbNbSr$_{1/2}$…) that is consistent with a Sr^{2+}-to-Nb^{5+} ratio on *B*-sites of B_{Sr}/B_{Nb}=1/2.[34]

Extended X-Ray Absorption Fine-Structure (EXAFS) Analysis: Representative Sr *K*-edge EXAFS data measured at a temperature of 20 K for *PZT:SNO-1* samples are shown in Figure 5 as a function of the photoelectron wave vector *k*. A Fourier transform of these EXAFS data produces peaks as a function of the scattering distance *r* (*x*-axis on Fourier transform) from the backscattering atoms, corresponding to scattering shells in the polycrystal (Figure 6).[25] However, phase shifts of the photoelectrons at both the absorbing and backscattering atoms or ions create shifts from the real bond length *R* for a given pair, as well as constructive and destructive interference.   Therefore, careful fitting with established scattering functions was required to extract quantitative local structure information. First, fits to SrTiO$_3$ (*STO*) data are described that help establish the overall scale factor S_0^2. Next, the efficacy of the fitting model for determining Sr *B*-site occupancy is tested on the *SNO* samples. Finally, the *PZT:SNO* fits are described.

Fits to the measured EXAFS data of the *STO* model compound gave results that are consistent with the expected perovskite structure. The pair-distance distribution variance σ^2 for the nearest Sr-O neighbors was fairly large and could not be explained solely by thermal vibrations, indicating a possible local lattice distortion that was not expected from X-ray crystallography. The typical overall scale factor for Sr *K*-edge EXAFS analysis is S_0^2=1.0;[35] however, the measured overall scale factor is S_0^2=1.35 for the present data (reproducible within ~5 %). This discrepancy is likely due to a correlation between the presence of a local lattice distortion and an enhanced overall scale factor in the fits. When the overall scale factor was fixed at S_0^2=1.0 in our EXAFS analysis and the resulting pair-distance distribution variance values were subsequently fit with a correlated Debye model,[36] we obtained the reasonable result that the Sr-O bond has a slightly enhanced non-thermal variance (i.e. static disorder) of 0.0020(7) Å^2, while the eight Sr-Ti bonds at $R\approx$3.4 Å and the six Sr-Sr pairs at $R\approx$3.9 Å possess

no measurable static disorder. Such a distortion would occur for a simple local rotation of the

[TiO$_{6/2}$]$^{2-}$ octahedra. Note that any such distortion must necessarily not possess long-range order,

since it has not been observed in diffraction experiments. More experimental EXAFS data,

particularly from the Ti *K*-edge, would be required to pursue this matter further. The thermal

parameters are otherwise consistent with previous measurements at the Ti *K*-edge[37] and are

typical based on our experience with manganese perovskites.[38]

According to previous investigations,[34] the *SNO* samples are expected to be substantially

distorted and possess a more complex structure relative to *STO* samples. In fact, the Fourier

transforms shown in Figure 6 reflect this situation. Distortions are expected not only in *SNO*

samples, but also in *PZT:SNO*. These distortions and the complicated nature of two-site fits

necessitate a fitting model to be developed for determining the fractional Sr *B*-site occupancy f_B,

and this model has been tested on the *SNO* samples. The fitting model is based on the *STO* and

Sr$_4$Nb$_2$O$_9$ structures,[34] in which the number of neighbors around each Sr^{2+} is determined by one

parameter, namely f_B. Most of the bond lengths were allowed to vary unconstrained to the ideal

structure and had substantially enhanced pair-distance distribution variance values of σ^2~0.03

Å^2. These enhanced σ^2 values indicate distortions in the *SNO* samples relative to an ideal

perovskite. The main differences between the *A*-sites and the *B*-sites in this structure are the

nearest-neighbor oxygen coordination and the identity of the nearest metal neighbor: The *A*-site

has 12 Sr(*A*)-O pairs at a bond length $R\approx2.94$ Å, followed by $8f_B$ Sr(*A*)-Sr(*B*) pairs and $8(1-f_B)$

Sr(*A*)-Nb (*B*) pairs at $R\approx3.59$ Å. The *B*-site, on the other hand, features 6 Sr(*B*)-O pairs at

$R\approx2.16$ Å and 8 Sr(*B*)-Sr(*A*) pairs at $R\approx3.59$ Å. For example, in Sr$_4$Nb$_2$O$_9$, the fraction of Sr^{2+} on

the *B*-site is f_B=0.25, and so the *A*-site has 2 Sr(*A*)-Sr(*B*) pairs at $R\approx3.59$ Å. Since the electron
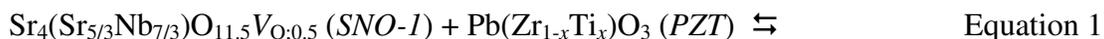
scattering amplitudes for Sr^{2+} and Nb^{5+} are very similar, the EXAFS data of the *SNO* samples are sensitive to the Sr *B*-site occupancy primarily through the nearest-neighbor oxygen peaks.
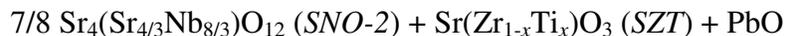
Using the above fitting model, the fraction of Sr^{2+} ions on the *B*-site was allowed to vary, but the overall scale factor was fixed to S_0^2=1.0 in fits to the *SNO* data. The quality of the fits is very good, considering these necessary assumptions and simplifications. For *SNO-1* and *SNO-2*, the following fractions of Sr^{2+} ions on *B*-sites are obtained by EXAFS analysis: $f_{B,\text{exp}}$(Sr)=32(2) % for Sr$_4$(Sr$_{5/3}$Nb$_{7/3}$)O$_{11.5}$V$_{O;0.5}$ (*SNO-1*) and $f_{B,\text{exp}}$(Sr)=33(2) % for Sr$_4$(Sr$_{4/3}$Nb$_{8/3}$)O$_{12}$ (*SNO-2*). Nominally, f_B(Sr)=29 % and f_B(Sr)=25 %, respectively, would be expected for *SNO-1* and *SNO-2*. The EXAFS errors were determined using a Monte Carlo method,[28] and primarily reflect errors in reproducibility. Comparisons to the nominal f_B values indicate that the systematic errors may be as large as 30 %.

In contrast to the *SNO* data, the *PZT:SNO* EXAFS data is sensitive to the Sr *B*-site occupancy both in the nearest-neighbor oxygen coordination and in the near-neighbor metal scattering peaks, because the scattering amplitudes of Pb^{2+} and Ti^{4+} cations contrast strongly with those of Sr^{2+}, Nb^{5+}, and Zr^{4+} cations. In addition, while *PZT* is distorted relative to the ideal perovskite structure,[3] the distortions are much simpler than in Sr$_4$Nb$_2$O$_9$.[34] The *PZT:SNO* fitting model is therefore based on the tetragonal *P4mm* structure of *PZT*,[3] rather than the ideal perovskite structure. Hence many distortions, which had to be modeled with an enhanced σ^2 in the *SNO* fits, are explicitly included, as will be seen below. These advantages should make the measurement of f_B even more reliable in *PZT:SNO* samples than in *SNO* samples. Although the distortions require more scattering shells to be included in the fit, the peak separation is generally quite good considering the different species in each shell. Although the number of varied parameters is relatively large at 23, this value is far below the number of 40 independent data points given by *Stern*'s rule.[39]
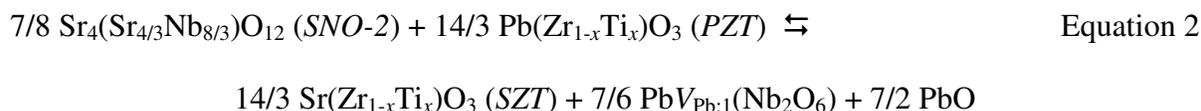
Figure 7 shows representative Sr *K*-edge EXAFS data for ceramic material *PZT:SNO-1*, together with two fits (see Table I for fit details). The measured σ^2 values (Table 1) are unusually small for the Sr(*B*)-Pb and Sr(*B*)-Ti pairs, most likely due to small differences between the real distortions and the fit model. Fits that constrain Sr^{2+} ions onto the Pb^{2+} site (*A*-site) do not reproduce the peak at $r \approx 3.3$ Å, while fits that allow 10±3 % of Sr^{2+} ions to occupy the Zr^{4+},Ti^{4+} site (*B*-site) reproduce the peak at $r \approx 3.3$ Å very well. The most prominent difference between these two fitting models is the presence of a Sr-Pb pair at $R \approx 3.42$ Å. In addition, other smaller peaks occurring at higher *r*-values are much better reproduced by the fit that allows 10±3 % of Sr^{2+} ions on the *B*-site. The measured *B*-site fraction for Sr^{2+} ions is well reproduced at all four measurement temperatures, and it is not sensitive to our choice of $S_0^2 = 1.0$. In addition, an *F*-test (*Hamilton* test)[40-42] considering structure models with different fractions of Sr^{2+} cations on *B*-sites, namely f_B(Sr)=10 % versus f_B(Sr)=0, rules out the latter with 99 % confidence. All the above mentioned findings are consistent and indicate very strongly that 10±3 % of the Sr^{2+} cations present in *PZT:SNO-1* occupy the nominal *B*-sites of the *PZT* host lattice.

Discussion of Defect Chemistry: The formal composition of solid solution *PZT:SNO-1* corresponds to $(PZT)_{0.995}(SNO\text{-}1)_{0.005}(PbO)_{0.01}$ or, more specifically, $[Pb(Zr_{0.52-0.53}Ti_{0.48-0.47})O_3]_{0.995}[Sr_4(Sr_{5/3}Nb_{7/3})O_{11.5}V_{O;0.5}]_{0.005}[PbO]_{0.01}$. This formula implies that ≈ 29.4 % (5/17) of Sr^{2+} cations occupy the octahedral *B*-sites in the perovskite-type *PZT* host lattice. Owing to the stronger basicity of SrO compared to PbO, the following chemical reaction between *PZT* and *SNO-1* has to be considered:

$$Sr_4(Sr_{5/3}Nb_{7/3})O_{11.5}V_{O;0.5} \ (SNO\text{-}1) + Pb(Zr_{1-x}Ti_x)O_3 \ (PZT) \ \leftrightarrows \qquad \text{Equation 1}$$

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$$7/8 \text{ Sr}_4(\text{Sr}_{4/3}\text{Nb}_{8/3})\text{O}_{12} \text{ } (\textit{SNO-2}) + \text{Sr}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3 \text{ } (\textit{SZT}) + \text{PbO}$$

The reaction shown in Equation 1 affords (i) strontium niobate *SNO-2* that is free of oxygen vacancies, (ii) strontium zirconium titanium oxide (*SZT*), and (iii) PbO as reaction products. *SNO-2* and *SZT* are taken up by or dissolved in the *PZT* matrix. After complete chemical reaction of *SNO-1* and *PZT* according to Equation 1, only ≈ 20.6 % (7/34) of Sr^{2+} cations would occupy the octahedral *B*-sites in the *PZT* host lattice of the corresponding solid solution, and no oxygen vacancies would exist. In addition, the subsequent chemical reaction shown in Equation 2 would give rise to complete vanishing of Sr^{2+} ions from nominal *B*-sites, along with the formation of lead vacancies V_{Pb} on *A*-sites:

$$7/8 \text{ Sr}_4(\text{Sr}_{4/3}\text{Nb}_{8/3})\text{O}_{12} \text{ } (\textit{SNO-2}) + 14/3 \text{ Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3 \text{ } (\textit{PZT}) \rightleftharpoons \qquad \text{Equation 2}$$

$$14/3 \text{ Sr}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3 \text{ } (\textit{SZT}) + 7/6 \text{ Pb}V_{\text{Pb;1}}(\text{Nb}_2\text{O}_6) + 7/2 \text{ PbO}$$

Based on the findings of our EXAFS analysis (see above), which indicated that 10 ± 3 % of the Sr^{2+} ions occupy the nominal *B*-sites in *PZT:SNO-1* solid solutions, and based on the chemical reactions between *SNO-1* and *PZT* (Equation 1) as well as *SNO-2* and *PZT* (Equation 2), the following chemical composition is derived for *PZT:SNO-1* after sintering and cooling:
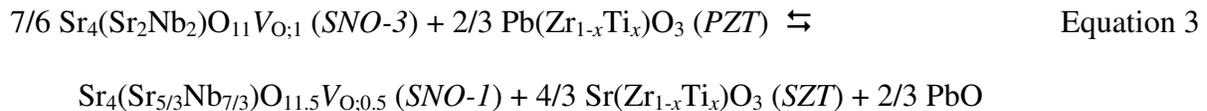
$$[\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3]_{0.973}[\text{Sr}_4(\text{Sr}_{4/3}\text{Nb}_{8/3})\text{O}_{12}]_{0.00213}[\text{Sr}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3]_{0.017}[\text{Pb}V_{\text{Pb}}(\text{Nb}_2\text{O}_6)]_{0.003}[\text{PbO}]_{0.029}$$

In *PZT:SNO-1*, a residual concentration of Sr^{2+} ions on the nominal *B*-sites is valence-compensated by Nb^{5+} ions in a typical cryolite-type configuration without the formation of oxygen vacancies. In addition, *SZT* and Pb(Nb$_2$O$_6$) that can be formed according to Equation 2

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are taken up and dissolved in the perovskite-type *PZT* host lattice. The chemical reaction according to Equation 2 implies the formation of lead vacancies V_{Pb} on *A*-sites. Another beneficial result of the solid-state reactions shown in Equations 1 and 2 is the *in situ* generation of PbO that can serve as sintering aid material for *PZT:SNO*.

The generation of PbO by acid-base reaction of *PZT* and *SNO*-dopant (Equation 1) is expected to be exothermic. During sintering at high temperature, the chemical equilibrium would therefore be shifted to the left-hand side, giving rise to the formation of oxygen vacancies. As shown in Equation 3, even the *SNO* compound according to Sr$_4$(Sr$_2$Nb$_2$)O$_{11}$$V_{O;1}$ (*SNO-3*), which corresponds to the extreme boundary composition of the non-stoichiometric range of the SrO-Nb$_2$O$_5$ phase diagram with cryolite-type structure,[31,32] can participate in the series of important temperature-dependent equilibrium reactions and therefore promote the formation of ferroelectric *PZT:SNO* solid solutions.

$$7/6 \ Sr_4(Sr_2Nb_2)O_{11}V_{O;1} \ (\textit{SNO-3}) + 2/3 \ Pb(Zr_{1-x}Ti_x)O_3 \ (\textit{PZT}) \ \leftrightarrows$$ Equation 3

$$Sr_4(Sr_{5/3}Nb_{7/3})O_{11.5}V_{O;0.5} \ (\textit{SNO-1}) + 4/3 \ Sr(Zr_{1-x}Ti_x)O_3 \ (\textit{SZT}) + 2/3 \ PbO$$

It has been an essential part of our piezoelectric materials design concept to intentionally induce temporary oxygen vacancies in the *PZT* host lattice of high-performance ferroelectric *PZT*-based solid solutions during thermal processing (esp. sintering) by means of doping with cryolite-type *SNO* in order to facilitate sintering and promote optimized microstructure formation. During post-sintering cooling of *PZT:SNO*, the temporary oxygen vacancies are substantially annihilated, essentially by shifting the equilibrium reactions shown in Equations 1-3 to the right-hand side and by re-filling with oxygen. These processes and the associated intricate

defect chemistry are crucial for the exceptional piezoelectric properties and the excellent stability

and degradation resistance exhibited by ferroelectric *PZT:SNO* solid solutions.

IV. Summary and Conclusion

New high-performance Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (*PZT*)-based ferroelectric solid solutions, denoted *PZT:SNO*, are described. They can be sintered at reasonably low temperatures ($T_S \leq 1100$ °C), exhibit excellent long-term stability and degradation resistance, and they give rise to exceptional piezoelectric properties. These properties are essentially achieved by controlling the material's defect chemistry, particularly by intentional generation of temporary oxygen vacancies in the *PZT* host lattice in order to facilitate sintering and promote optimized microstructure formation. Key to our material design concept are dopants based on cryolite-type strontium niobate (*SNO*) according to the general formula Sr$_4$(Sr$_{2-2y/3}$Nb$_{2+2y/3}$)O$_{11+y}$V$_{O,1-y}$ with $0 \leq y \leq 1$. The microscopic structure of ferroelectric perovskite-type *PZT:SNO* was investigated in particular by EXAFS analysis, which served as a powerful method to study the crystal lattice site occupancy of Sr^{2+} ions in *PZT:SNO* samples as well as in SrTiO$_3$ and *SNO* model and reference compounds. In *PZT:SNO*, Sr^{2+} ions with coordination numbers of $CN_{Sr}=12$ (*A*-site occupancy) and $CN_{Sr}=6$ (*B*-site occupancy) coexist. Our EXAFS analyses revealed that a remarkable portion of 10±3 % of the Sr^{2+} ions occupy the nominal *B*-sites (Zr^{4+},Ti^{4+} sites) in the perovskite-type *PZT* host lattice of *PZT:SNO-1* samples. This result is supported by EXAFS analyses of both a canonical SrTiO$_3$ perovskite and two *SNO* compounds, namely Sr$_4$(Sr$_{5/3}$Nb$_{7/3}$)O$_{11.5}$V$_{O;0.5}$ (*SNO-1*) and Sr$_4$(Sr$_{4/3}$Nb$_{8/3}$)O$_{12}$ (*SNO-2*), which served as model and reference materials. In addition, fit models that did not include Sr^{2+} ions on *B*-sites were ruled out by an *F*-test (*Hamilton* test). The clear presence of a Sr-Pb peak in the Fourier transformed EXAFS data of *PZT:SNO* samples served as further visual and qualitative confirmation of this structural model.

The generation of temporary oxygen vacancies and the intricate defect chemistry, both of which are induced and controlled by *SNO*-doping of *PZT*, are crucial for the exceptional piezoelectric properties and the excellent stability and degradation resistance exhibited by

PZT:SNO solid solutions. To the best of our knowledge, the results described in this research work

constitute the first published experimental verification for substantial *B*-site occupancy of Sr^{2+} ions in

PZT-based ferroelectric solid solutions.

V. Acknowledgments and Support

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VII. Figure Captions

Figure 1:   Ideal perovskite-type *ABO*$_3$ structure of SrTiO$_3$ (*STO*). The red spheres at the corners of the cube represent Sr^{2+} ions on *A*-sites, the white sphere at the center represents Ti^{4+} ions on *B*-sites, and the blue spheres represent oxygen. Sr^{2+} ions on the *A*-site are surrounded by the faces of [TiO$_{6/2}$]$^{2-}$ octahedra and therefore possess 12 immediate oxygen neighbors (so-called Sr(*A*)-O neighbors). The coordination number of Sr^{2+} in SrTiO$_3$ is hence *CN*$_{Sr}$=12.

Figure 2:   Representative XRD pattern (black line) and Rietveld simulation (magenta line) of *PZT:SNO-1* (Pb(Zr$_{0.53-0.52}$Ti$_{0.47-0.48}$)O$_3$ doped with ~0.5 mol-% of *SNO-1* = Sr$_4$(Sr$_{5/3}$Nb$_{7/3}$)O$_{11.5}$*V*$_{O,0.5}$). The orange line indicates the balance curve of XRD intensity$_{measured}$ (black line) minus XRD intensity$_{calculated}$ (magenta line). The expected splitting of XRD reflections according to rhombohedral crystal distortion (Bragg reflections indicated by green squares) and tetragonal crystal distortion (Bragg reflections indicated by blue triangles) in the ferroelectric state of *PZT* near the morphotropic phase boundary is clearly resolved.

Figure 3a: Schematic of the cryolite-type unit cell of Sr$_8$(Sr$_{10/3}$Nb$_{14/3}$)O$_{23}$*V*$_{O;1}$ (that is, two unit cells of *SNO-1* = Sr$_4$(Sr$_{5/3}$Nb$_{7/3}$)O$_{11.5}$*V*$_{O,0.5}$). The octahedral *B*-sites are predominantly occupied by Sr^{2+} ions (yellow spheres) and Nb^{5+} ions (white spheres) in alternating sequence. The blue spheres represent oxygen and *V*$_O$ represents an oxygen vacancy. It is apparent that Sr^{2+} ions residing on *B*-sites (yellow spheres) possess coordination number *CN*$_{Sr}$=6.

Figure 3b: Portion of the upper right region of the unit cell displayed in Figure 3a, indicating the close relationship of the cryolite-type structure shown in Figure 3a with the perovskite-type *ABO*$_3$ structure shown in Figure 1. The red spheres represent Sr^{2+} ions on *A*-sites, the yellow

spheres represent Sr^{2+} ions on *B*-sites, the white spheres represent Nb^{5+} ions on *B*-sites, and the

blue spheres represent oxygen. Please note that the octahedral *B*-sites are occupied by Sr^{2+} ions

(yellow spheres) and Nb^{5+} ions (white spheres) in alternating sequence. It is apparent that Sr^{2+}

ions residing on *A*-sites (red spheres) possess coordination number CN_{Sr}=12.

Figure 4:   Representative XRD pattern (black line) and Rietveld simulation (magenta line)

of oxygen deficient cryolite-type dopant *SNO-1* = Sr$_4$(Sr$_{5/3}$Nb$_{7/3}$)O$_{11.5}$V$_{O,0.5}$. The orange line

indicates the balance curve of XRD intensity$_{measured}$ (black line) minus XRD intensity$_{calculated}$

(magenta line). The positions of expected Bragg reflections for the cryolite-type structure are

indicated by blue triangles.

Figure 5:   EXAFS Sr *K*-edge data acquired for *PZT:SNO-1* = (*PZT*)$_{0.995}$(*SNO-1*)$_{0.005}$(PbO)$_{0.01}$

in fluorescence mode for 1 scan (data acquisition time: ~30 min) and 17 scans (data acquisition

time: ~7.5 h) as an example of the data quality. The EXAFS Sr *K*-edge data quality of the model

compounds was much higher.

Figure 6:   Plot of Fourier transforms (FT) of $k^2\chi(k)$ *vs. r* of EXAFS data for SrTiO$_3$ (*STO*),

Sr$_4$(Sr$_{5/3}$Nb$_{7/3}$)O$_{11.5}$V$_{O;0.5}$ (*SNO-1*), Sr$_4$(Sr$_{4/3}$Nb$_{8/3}$)O$_{12}$ (*SNO-2*), and (*PZT*)$_{0.995}$(*SNO-1*)$_{0.005}$

(PbO)$_{0.01}$ (*PZT:SNO-1*).

Figure 7:   Plot of Fourier transform (FT) of $k^2\chi(k)$ *vs. r* for *PZT:SNO* and corresponding

data fits. It is evident that the fit (dotted line) in which Sr^{2+} ions are constrained onto the Pb^{2+}

(*A*)-site does not reproduce the data peak (continuous line) at $r\approx$3.3 Å, while the fit (dashed line)

that allows 10±3 % of Sr^{2+} ions on the Zr^{4+},Ti^{4+} (*B*)-site reproduces the data peak at *r*≈3.3 Å very

well. Other peaks at higher *r*-values are also better reproduced by the latter fit. The Sr^{2+} *B*-site

fraction of 10±3 % is well reproduced at the different EXAFS measurement temperatures.

VIII. Tables

Table 1:   Fit Results for EXAFS Analysis of *PZT:SNO-1* Samples.[a]

		f_B(Sr)=0[b]			f_B(Sr) varying[b]		
	R_{diff}[c]	σ^2 [Å^2][d]	R [Å][e]	N[f]	σ^2 [Å^2][d]	R [Å][c]	N[f]
Sr(*A*)-O	2.559	0.008(6)	2.6(1)	4.0	0.005(3)	2.63(2)	3.6
Sr(*A*)-O	2.892	0.010	2.76(3)	4.0	0.00654	2.77(2)	3.6
Sr(*A*)-O	3.273	0.012	3.35(7)	4.0	0.00826	3.41(6)	3.6
Sr(*A*)-Zr	3.418	0.007(1)	3.27(2)	4.0	0.009(1)	3.26(1)	3.6
Sr(*A*)-Ti	3.418	0.01042	3.35(2)	4.0	0.01284	3.39(3)	3.6
Sr(*A*)-Pb	4.046	0.022(9)	4.12(4)	6.0	0.013(4)	4.12(4)	5.4
Sr(*A*)-Pb	5.722	0.01(10)	6(1)	12.0	0.01(6)	5.92(5)	10.8
Sr(*B*)-O	1.845	-	-	-	0.00160	1.73(8)	0.1
Sr(*B*)-O	2.046	-	-	-	0.00250	1.96(3)	0.5
Sr(*B*)-O	2.295	-	-	-	0.00360	2.19(8)	0.1
Sr(*B*)-Pb	3.418	-	-	-	0.0005(8)	3.37(1)	0.8
Sr(*B*)-Zr	4.046	-	-	-	0.0000(1)	4.10(3)	0.3
Sr(*B*)-Ti	4.046	-	-	-	0.00000	3.77(4)	0.3
Sr(*B*)-Zr	5.722	-	-	-	0.004(8)	5.52(8)	0.6
Sr(*B*)-Ti	5.722	-	-	-	0.00587	5(1)	0.6
ΔE_0[g]		-8(2)			-1(1)		
f_B(Sr)[b]		0.0			0.10(3)		
dof[h]		28.4			16.4		
R [%][j]		30.2			15.8		

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Footnotes for Table 1:

[a]: The EXAFS data was measured at a temperature of 20 K. The fit range was 1.20-6.00 Å. The k^2-weighted data was Fourier transformed between 2.50-15.00 Å^{-1} and Gaussian narrowed by 0.30 Å^{-1}. The overall scale factor was fixed to S_0^2=1.0 for these fits. The second Sr(A)-O pair σ was constrained to be 0.01 Å greater than the first, as was the third Sr(A)-O pair σ constrained to the second. The Sr(B)-O pairs were similarly constrained. The Sr-Ti pair-distance distribution variance values σ^2 were constrained to (μ_{Sr-Zr}/μ_{Sr-Ti})σ_{Sr-Zr}^2 at the same or similar distance, where μ_X is the reduced mass of the X scattering pair. Reported errors shown in parenthesis were determined by a Monte-Carlo method and do not reflect systematic errors (see Ref. 28).

[b]: Fraction of Sr^{2+} cations on the nominal B-sites.

[c]: Expected bond length from respective A- and B-sites determined from diffraction measurements of *PZT* (see Ref. 3).

[d]: Pair-distance distribution variance.

[e]: Atomic distance from respective A-sites or B-sites.

[f]: Number of neighbors per Sr^{2+} ion (see Ref. 3).

[g]: ΔE_0 is the overall shift in the value of E_0 chosen for determining the photoelectron wave vector k.

[h]: Fit degrees of freedom, determined using *Stern*'s rule (see Ref. 39) for the number of independent data points.

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j: $R[\%] = \dfrac{\sum\limits_{i} (\tilde{\chi}_{R,i} - \tilde{F}_{R,i})^2 + (\tilde{\chi}_{I,i} - \tilde{F}_{I,i})^2}{\sum\limits_{i} \tilde{\chi}_{R,i}{}^2 + \tilde{\chi}_{I,i}{}^2}$, where $\tilde{\chi}_R, \tilde{\chi}_I, \tilde{F}_R, \tilde{F}_I$ are the real and imaginary

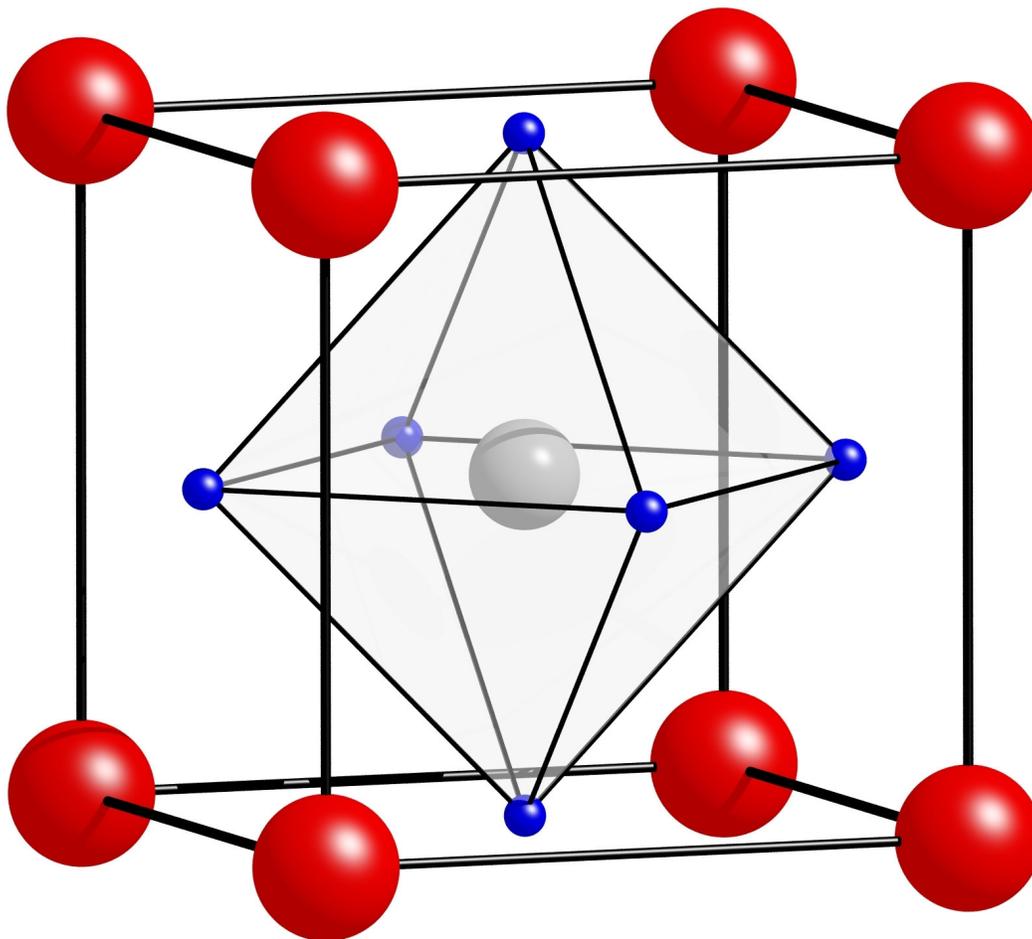parts of the Fourier transform of $\chi(k)$ and the fit, respectively.

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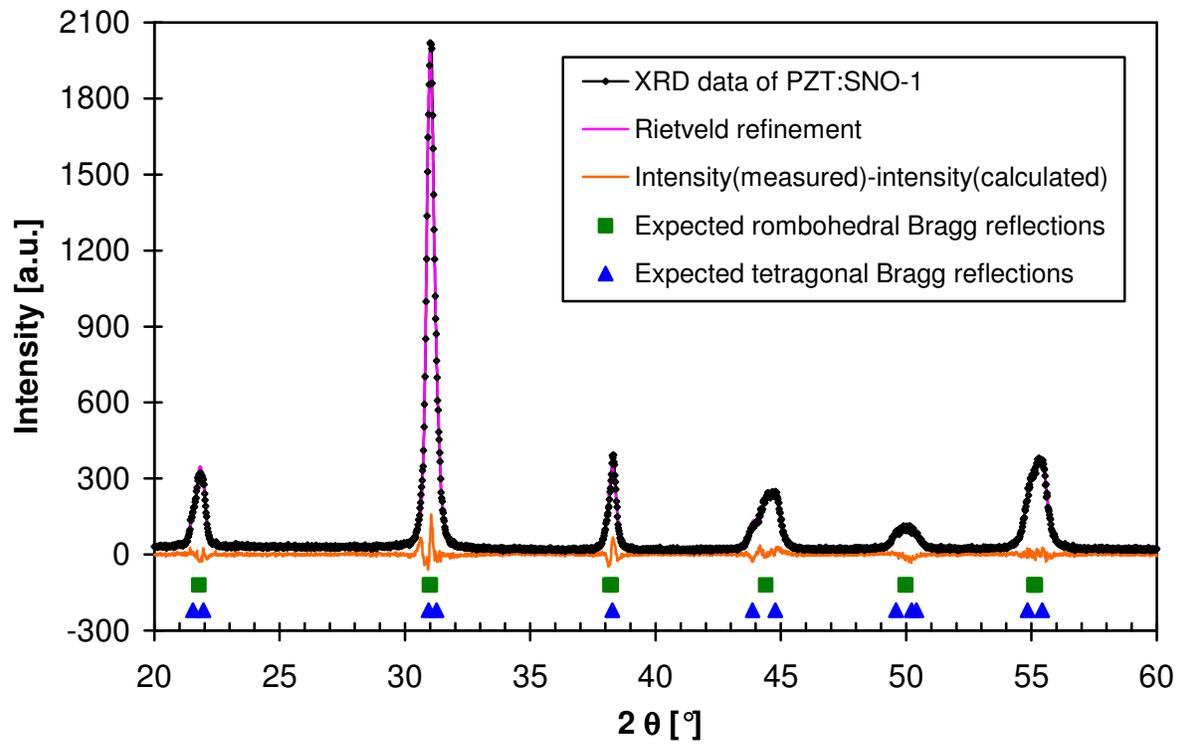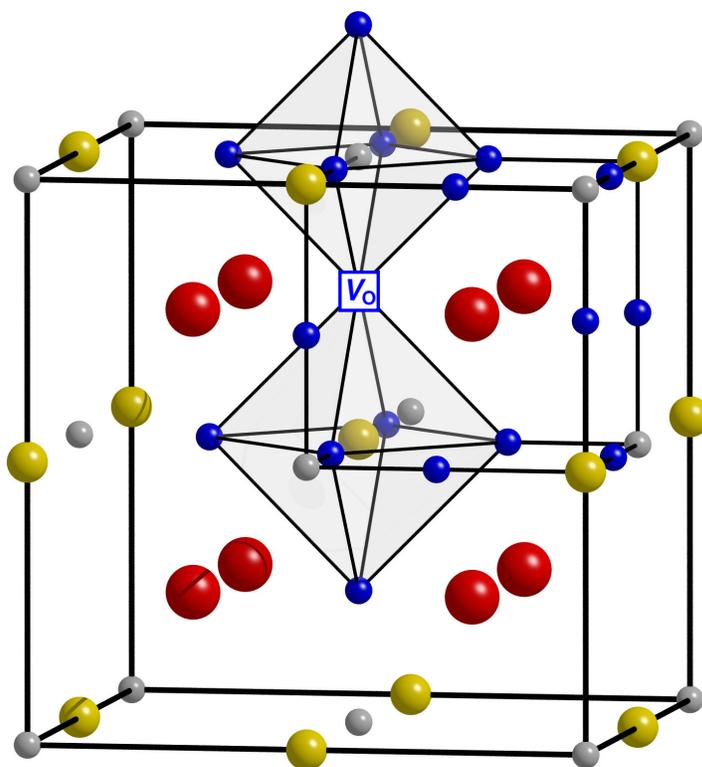"Remarkable Strontium *B*-Site Occupancy in Ferroelectric Pb(Zr$_{1-x}$Ti$_x$)O$_3$ Solid Solutions Doped with Cryolite-Type Strontium Niobate"

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IX. Figures

Figure 1

"Remarkable Strontium *B*-Site Occupancy in Ferroelectric Pb(Zr$_{1-x}$Ti$_x$)O$_3$ Solid Solutions Doped with Cryolite-Type Strontium Niobate"

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Figure 2

"Remarkable Strontium _B_-Site Occupancy in Ferroelectric Pb(Zr$_{1-x}$Ti$_x$)O$_3$ Solid Solutions Doped with Cryolite-Type Strontium Niobate"

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Figure 3a

"Remarkable Strontium *B*-Site Occupancy in Ferroelectric $Pb(Zr_{1-x}Ti_x)O_3$ Solid Solutions Doped with Cryolite-Type Strontium Niobate"

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Figure 3b

"Remarkable Strontium *B*-Site Occupancy in Ferroelectric Pb(Zr$_{1-x}$Ti$_x$)O$_3$ Solid Solutions Doped with Cryolite-Type Strontium Niobate"

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Figure 4

"Remarkable Strontium *B*-Site Occupancy in Ferroelectric Pb(Zr$_{1-x}$Ti$_x$)O$_3$ Solid Solutions Doped with Cryolite-Type Strontium Niobate"

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Figure 5

"Remarkable Strontium *B*-Site Occupancy in Ferroelectric Pb(Zr$_{1-x}$Ti$_x$)O$_3$ Solid Solutions Doped with Cryolite-Type Strontium Niobate"

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Figure 6

"Remarkable Strontium *B*-Site Occupancy in Ferroelectric Pb(Zr$_{1-x}$Ti$_x$)O$_3$ Solid Solutions Doped with Cryolite-Type Strontium Niobate"

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Figure 7