Experimental and theoretical study of crystal structure and lattice dynamics of $SrTi_{1-x}Mn_xO_3$ perovskite

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The $SrTi_{1-x}Mn_xO_3$ ceramics were studied experimentally by X-ray diffraction (XRD) and infrared spectroscopy; the results were compared with theoretical DFT calculation. It is well known that $SrTiO_3$ undergoes antiferrodistortive phase transition to tetragonal phase at T_C = 105 K. This T_C should decrease with Mn concentration. We performed low-temperature XRD studies down to 10 K, but unfortunately we did not observe any structural phase transition in $SrTi_{1-x}Mn_xO_3$ with x=0.1, 0.2 and 0.3.

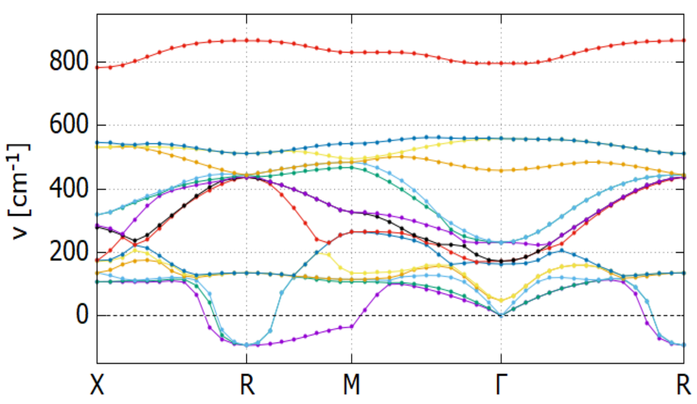
Samples

The **$SrTiO_3$** (STO) ceramic was prepared by **S. Hoffmann-Eifert** using a conventional mixed-oxide route. The starting substance was high-purity $SrCo_3$ and fine grained TiO_2 powder. The stoichiometry of the samples was modified to $Sr_{1.000}Ti_{1.001}O_3$ by mixing of the right amounts of precursor powders and the substance was subsequently mixed in a cyclohexanolic suspension for 1 hour, ball milled for 3 hours and calcined at 1050 °C for 18 hours. Cold-pressed cylinders of $SrTiO_3$ were sintered at 1380 °C for 7 hours.
The **$SrTi_{1-x}Mn_xO_3$** ceramics (**x=0.1, 0.2** and **0.3**) were made by **Bogdan Dabrowski** using a two-step solid-state method. In first step, hexagonal precursor materials were synthesized in flowing H2/Ar gas at temperatures 1300 °C to obtain single-phase oxygen-reduced perovskite samples. After that the samples were annealed in oxygen at 350 °C which resulted in in stabilization of cubic perovskite structure and oxygen stoichiometry of 3.00 ± 0.002.
All the samples were further polished.

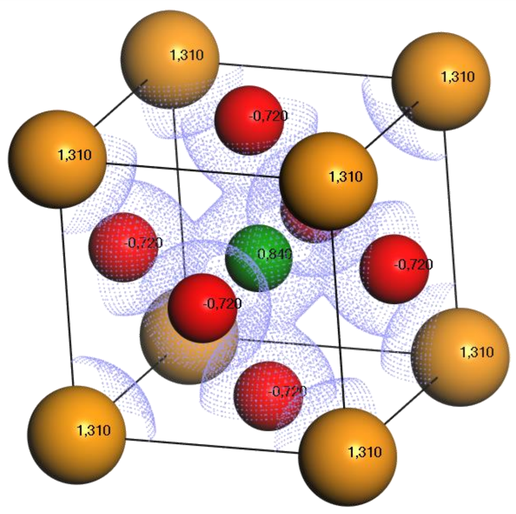
Ab initio calculations

The calculations of **phonon dispersion curves** of **STO** were performed by DFT methods implemented in **CASTEP** module of **Materials Studio 8.0**. The setting were as follows: Ultra-fine quality was chosen with adjustment of cut-off energy E_{cutoff} to value 1000 eV which was determined by the quite simple algorithm: the E_{cutoff} was changed and total energy of the system was checked. Once there was no oscillations and big difference in total energy with increasing cut-off energy from certain value, this value was taken as sufficient.
With the same algorithm k-sampling was chosen as 8x8x8. Functional was selected as LDA CA-PZ and in electronic setting was selected norm-conserving pseudopotentials. The phonon dispersion were calculated by linear response method.

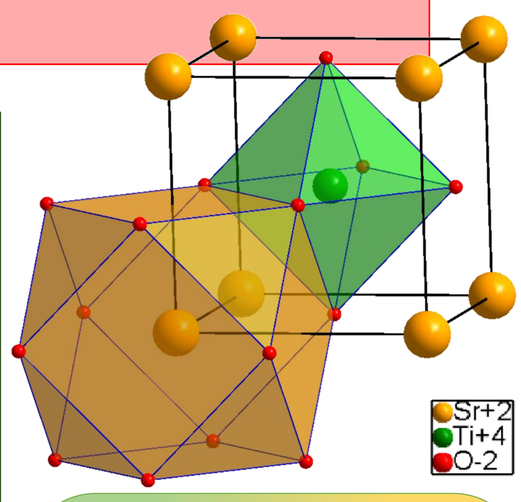
The **lattice parameters** of **$SrTi_{1-x}Mn_xO_3$** were calculated by **Quantum ESPRESSO** program with Burai graphical interface (S. Nishihara) using GGA approach. The cubic supercell contains 8 Ti/Mn atoms.



Calculated phonon spectra of STO with LO-TO splitting. Phonon softening at the R point can be seen. It is well known that this phonon softening causes structural (antiferrodistortive) phase transition at temperature 105 K from cubic to tetragonal symmetry.



Subsurface of electronic density for the value of 0.45 electrons/Å³ STO. One can see that continuous surface between Ti and O testifies about more covalent bond than between Sr and O, where applies rather ionic bond. Mulliken charges are displayed.

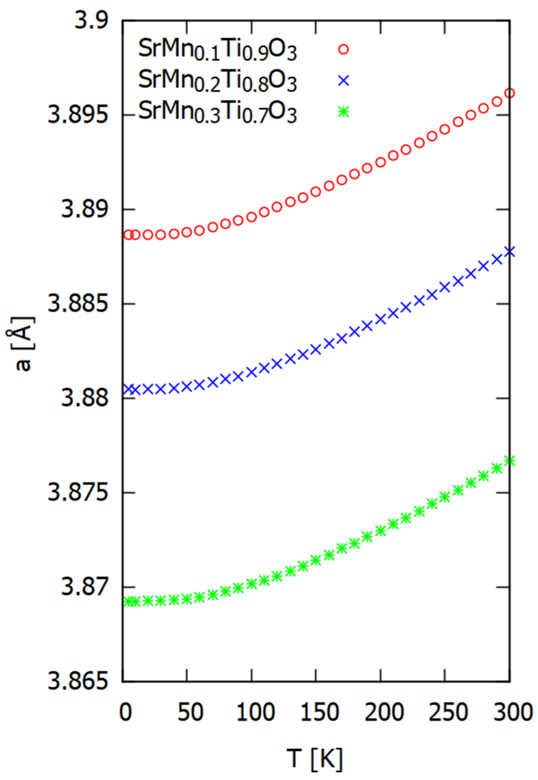


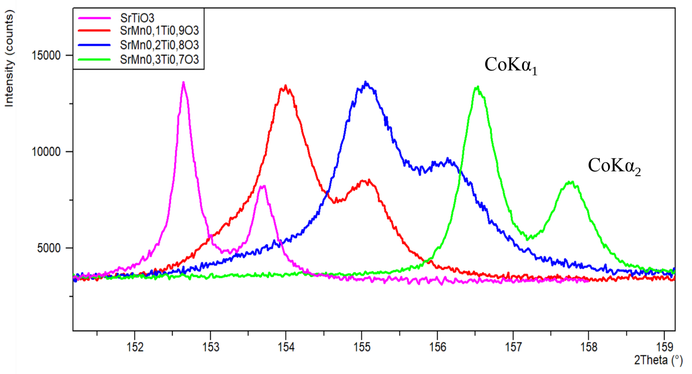
Comparison for STO between frequency of calculated phonons at gamma point from DFT and experimentally measured phonons from IR spectroscopy. Δf means relative deviations from measured value. It can be seen that good agreement was achieved.

DFT	Δf [%]	IR spectr.
TO v [cm-1]		**TO v [cm-1]**
561	2.8	546
187	5.7	177
110	4.8	105
LO v [cm-1]		**LO v [cm-1]**
795	0.8	789
458	-3.6	475
175	1.7	172

X-ray diffraction

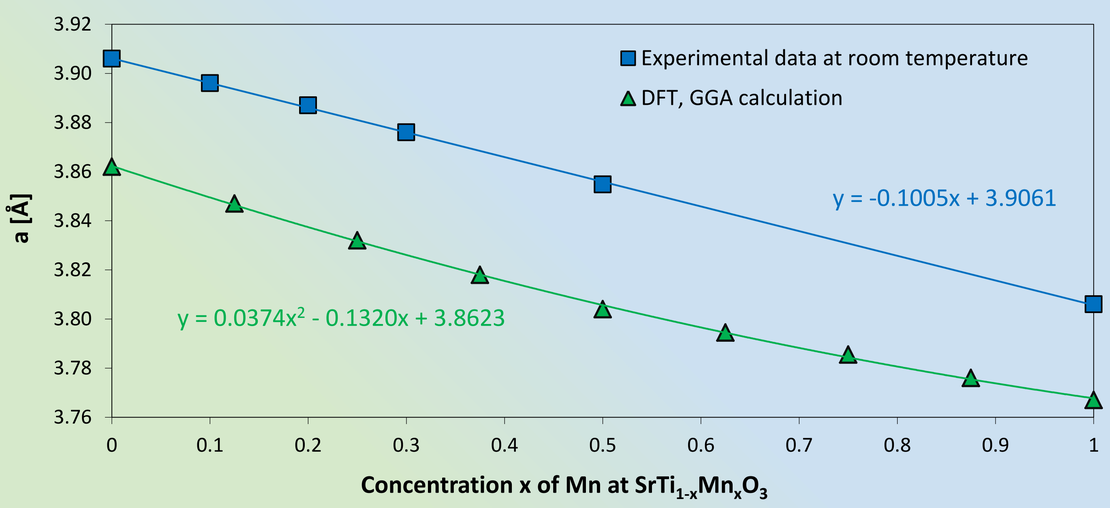
Experimental values of lattice parameters were measured in the Bragg-Brentano on diffractometer **X'Pert PRO PANalytical** with $CoK\alpha_{1,2}$ radiation and on a custom adapted Siemens D500 diffractometer equipped with a closed cycle Sumitomo Heavy Industries cryocooler with he $CuK\alpha_{1,2}$ radiation. The lattice parameters were determined by Pawley mode in the Rietveld analysis using the Topas software.





Diffractions from planes (330)/(411) at room temperature. The shift of diffraction angle to higher values with increasing concentration of Mn proves the decreasing of lattice parameter.

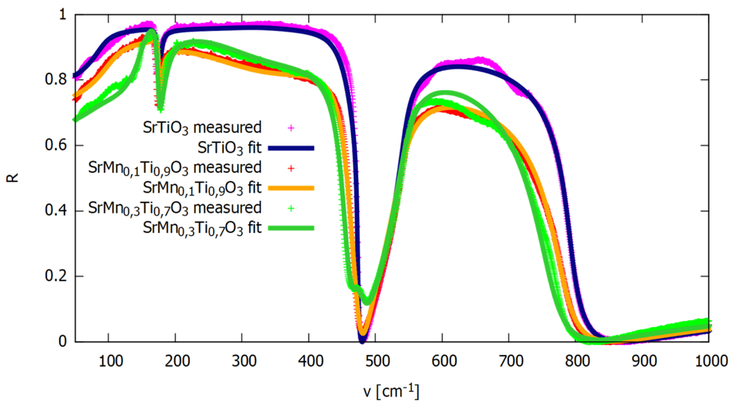
Temperature dependence of the lattice parameters in the $SrMn_xTi_{1-x}O_3$, x= 0.1, 0.2 and 0.3. We was expecting the structure phase transition to tetragonal similar close to STO at Tc = 105 K, but no structural phase transition was observed. According to the measured data, the possible tetragonal distortion should be smaller then 0.0004 Å. The tetragonal distortion in $SrTiO_3$ is by one order higher, ca. 0.004 Å.



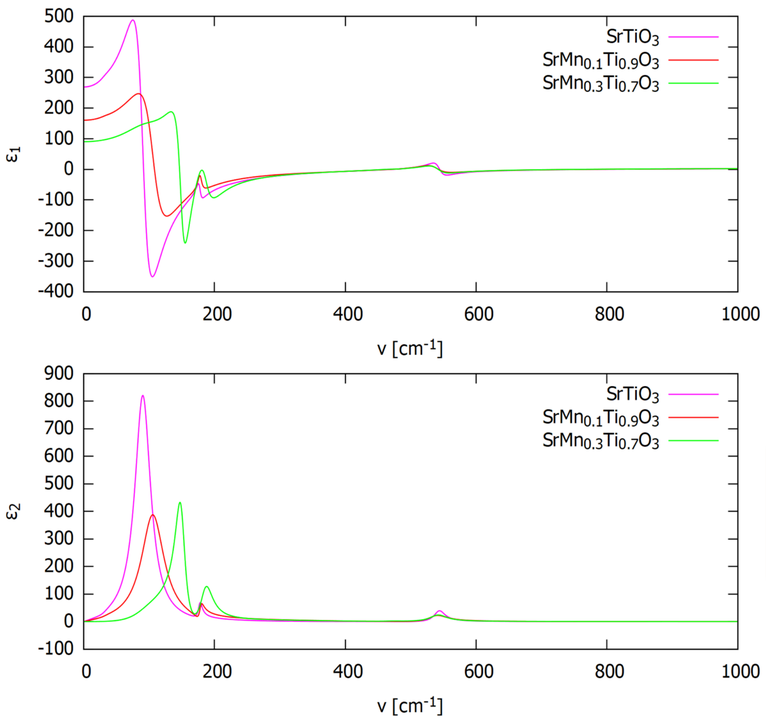
Experimental and theoretical lattice parameters. The linear decrease with increasing Mn was observed in the experimentally measured lattice parameters at room temperature. The theoretical lattice parameters calculated by DFT show also almost linear decrease, but the relative deviations from experimentally measured values are smaller than 1.5%.

Infrared spectroscopy

The spectroscopic experiments were performed using **FTIR spectrometer Bruker IFS 113v**. The measured reflectivity spectra were fitted using the **four-parameter model of the damped oscillators**.



Reflectivity spectra fitted with four-parametric model of damped oscillators. Each sample has three reflectivity bands. Three TO phonons are excited at the Γ point for each material. In $SrTi_{0.7}Mn_{0.3}O_3$, additional one phonon was observed at 186 cm^{-1}. The soft mode frequency increases with Mn concentration and therefore the permittivity decreases with rising x.



The real part of complex permitivity obtained from four-parametric model of damped socillators.

The imaginary part of complex permitivity obtained from four-parametric model of damped socillators.

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