Nanodomain states of strontium ferrites and their structural transformations

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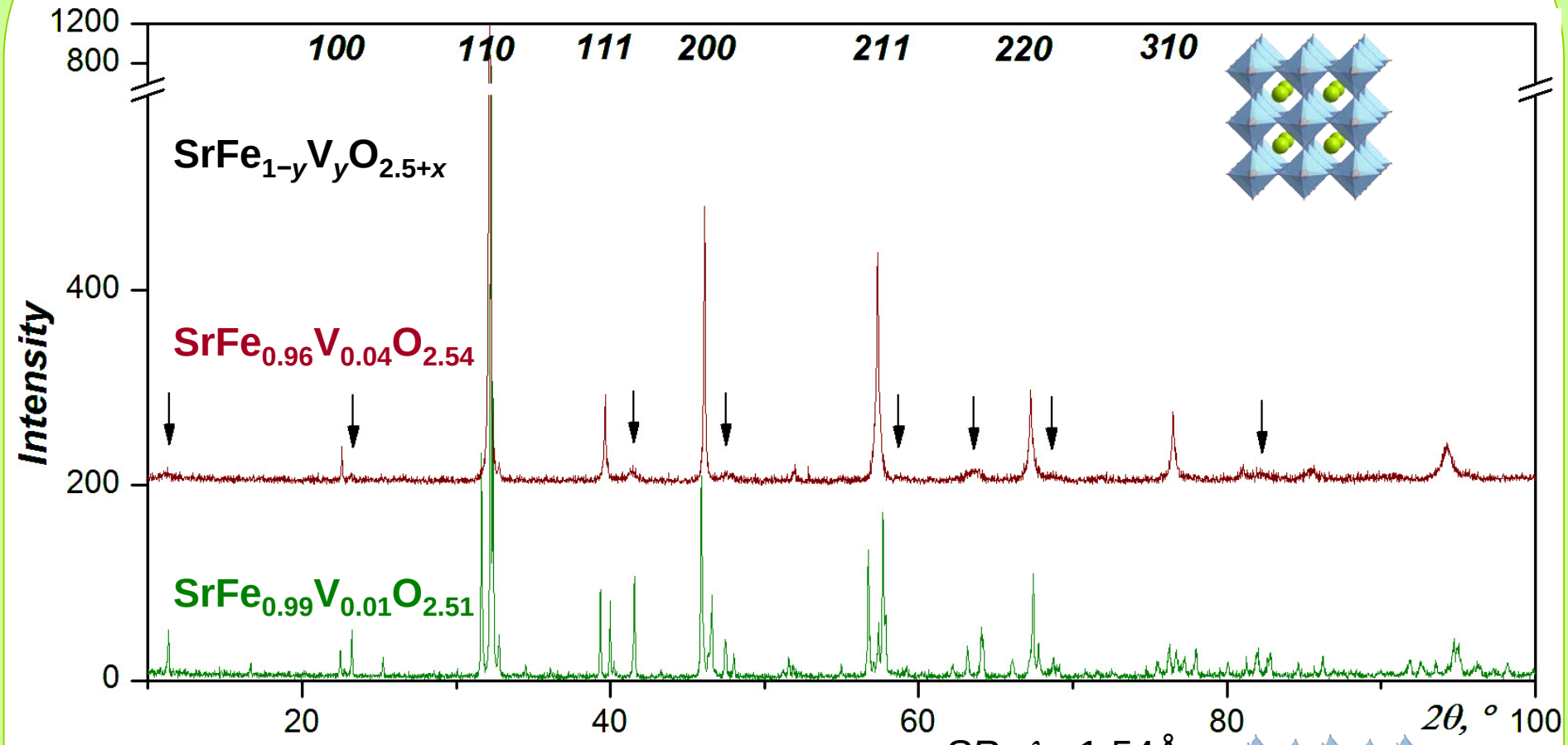
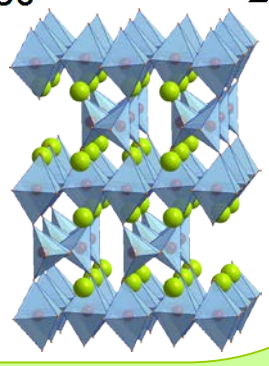
Synchrotron and Free electron laser Radiation: generation and application July 06 2016

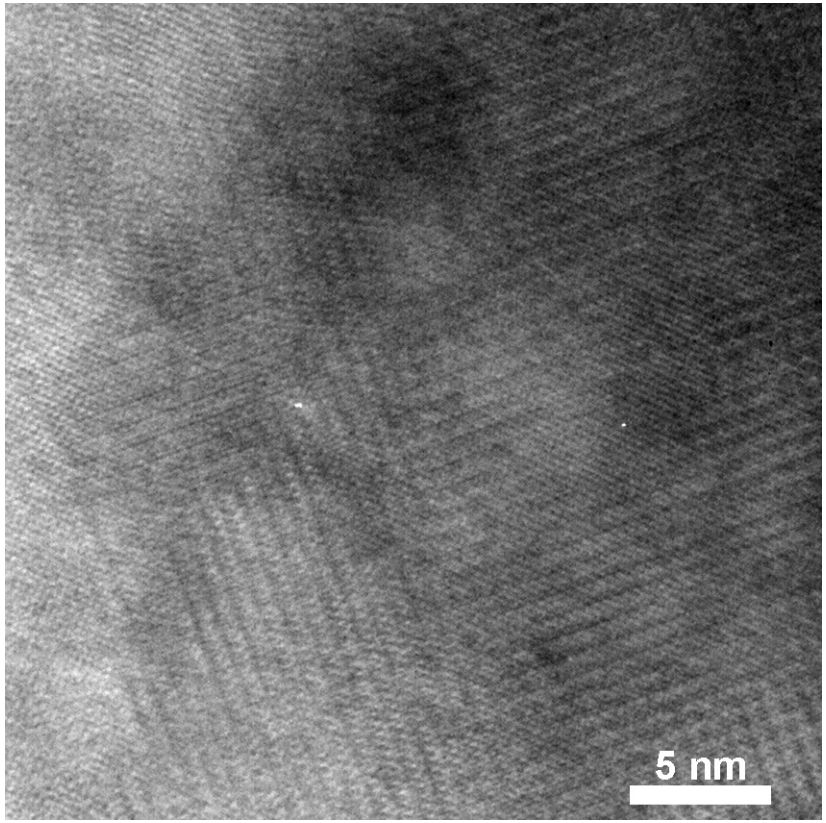
Strongly-non-stoichiometric perovskite-like oxides $SrFeO_{3-\delta}$



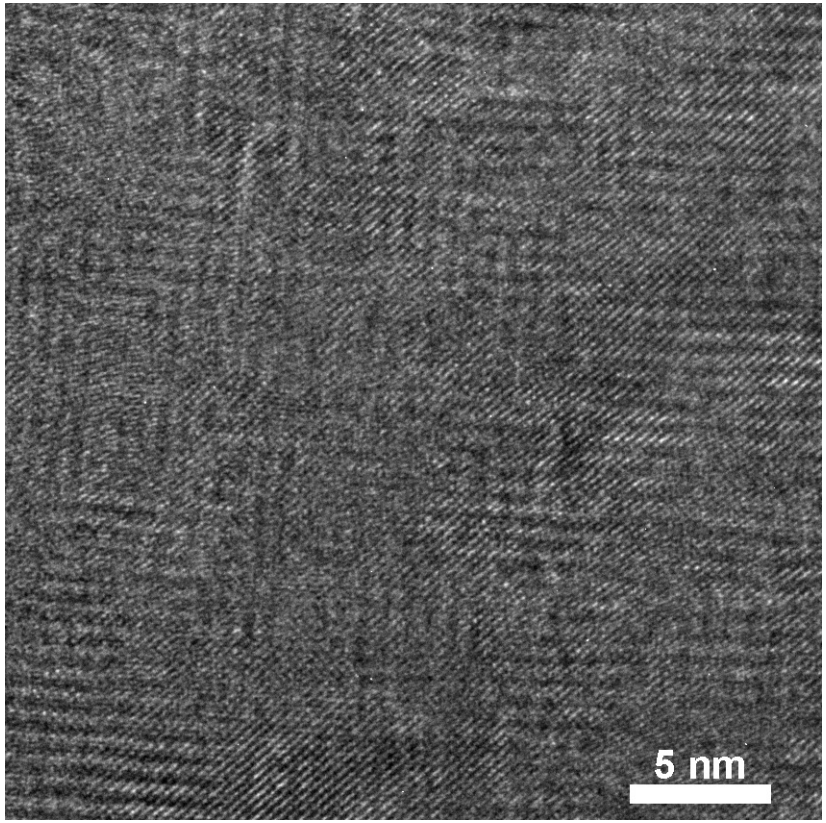


$Sr(Fe_{1-y}V_y)O_{2.5+x}$
$Sr(Fe_{1-y}Mo_y)O_{2.5+x}$
$Sr(Co_{0.8}Fe_{0.2})O_{2.64}$
$(Sr_{0.7}La_{0.3})(Co_{0.5}Al_{0.3}Fe_{0.2})O_{2.54}$
$Sr(Co_{0.75}Nb_{0.05}Fe_{0.2})O_{2.45}$
$Sr(Co_{0.7}Nb_{0.1}Fe_{0.2})O_{2.47}$

Strongly-non-stoichiometric perovskite-like oxides $SrFeO_{3-\delta}$



$SrFe_{0.95}Mo_{0.05}O_{2.5+x}$



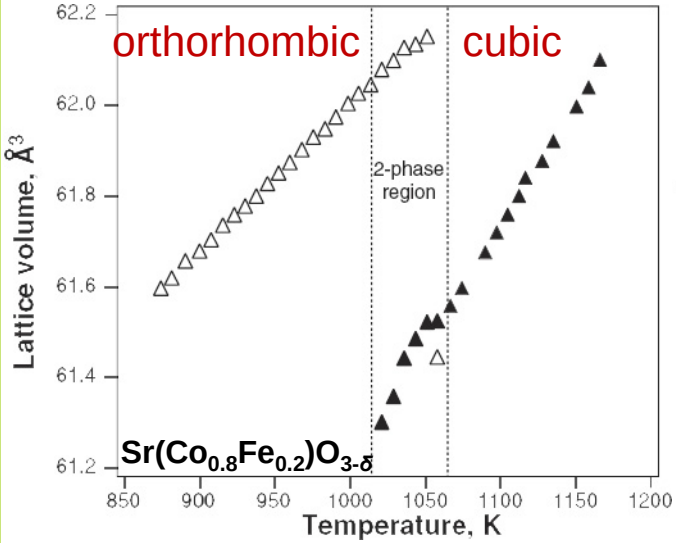
$SrFe_{0.92}Mo_{0.8}O_{2.5+x}$

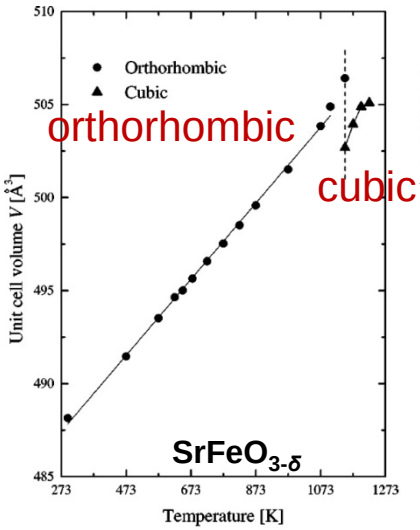
[Lindberg F. et. al. // J. Solid State Chem. 2004. 177. 1592]
[Doorn R. H. E. et. al. // Solid State Ionics. 2000. 128. 65]
[Liu Y. et al. // J. Solid State Chem. 2003. 170. 247]
[Nakayama N. et al. // J. Solid State Chem. 1987. 71. 403]
[Alario-Franco M.A. et al. // Materials Res. Bull. 1982. 17. 733]
[D'Hondt H. et al. // J. Solid State Chem. 2009. 182. 356]

$Sr_2Co_{2-x}Al_xO_5$
$La_{1-x}Sr_xCoO_{3-\delta}$
$(Ba_{1-x}La_x)_2In_2O_{5+x}$
$SrFe_{1-x}V_xO_{2.5+x}$
$Sr_xNd_{1-x}FeO_{3-y}$
$Sr_2Al_{0.78}Mn_{1.22}O_{5.2}$

Nano-domain state at low pO_2 improves mechanical stability of membranes

"order-disorder" phase transition:
abrupt change in lattice volume





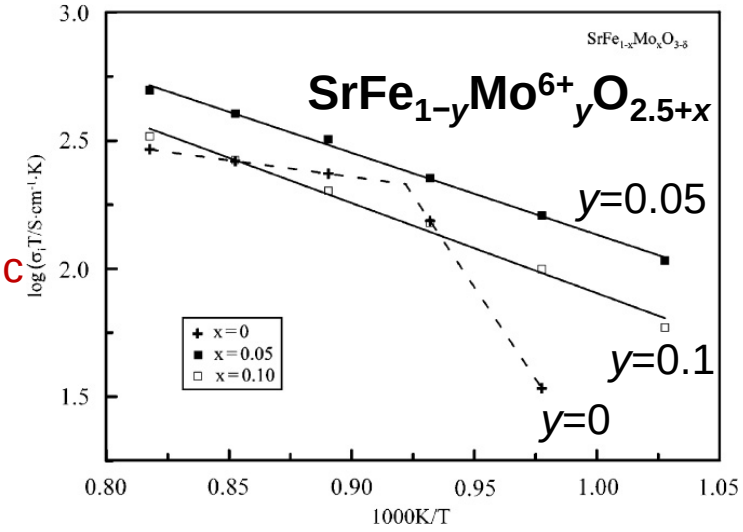
[McIntosh S. et al // Solid State Ionics. 2006. 177. 833.]

[Schmidt M. et al // J. Solid State Chem. 2001. 156. 292.]

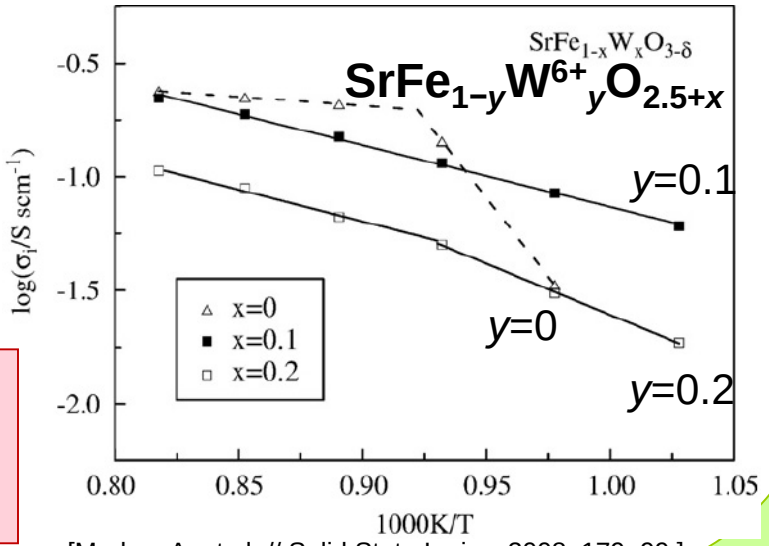
cracks

[Pei S. et al // Catalysis Letters. 1995. 30. 201.]

Arrenius plots for oxygen ion conductivity



[Markov A. et al // Solid State Ionics. 2008. 179. 1050.]



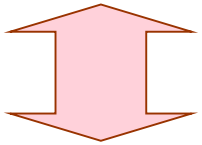
[Markov A. et al. // Solid State Ionics. 2008. 179. 99.]

Doping with high-charged cations leads to the formation of the system outside the homogeneity region of brownmillerite structure

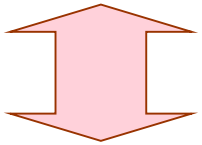
Structure investigations

To find correlations between **configuration of nanodomain** structure in strongly non-stoichiometric oxygen deficient oxides based in strontium ferrite $SrFeO_{3-\delta}$ and accompanying them specific **diffraction effects**

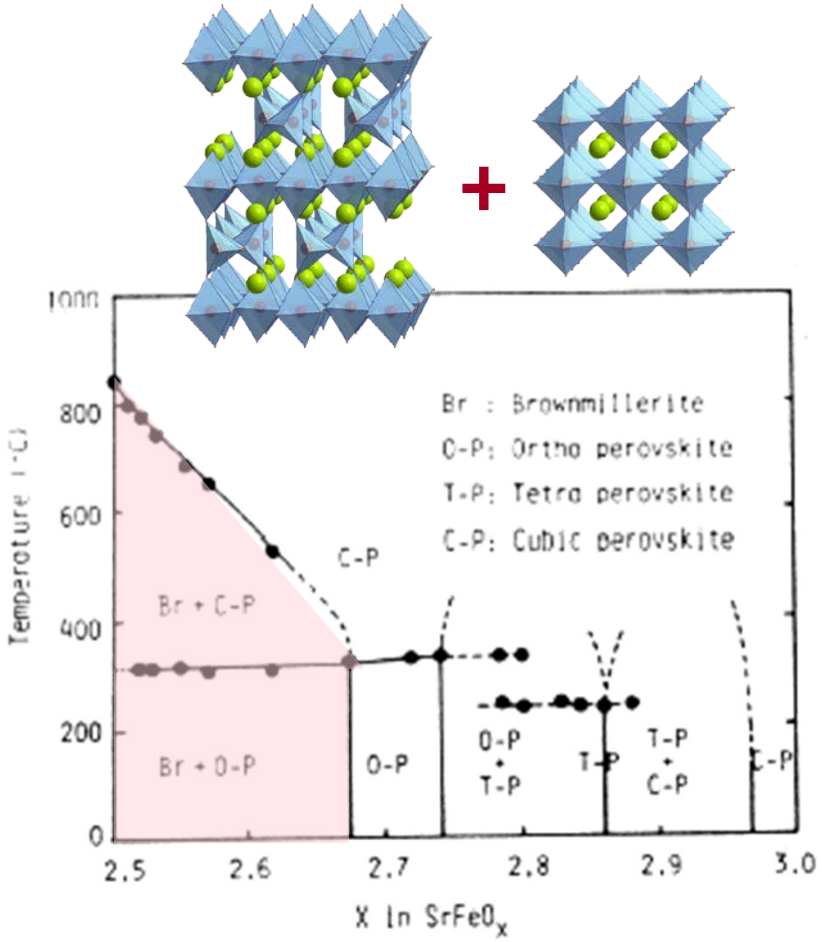
- cation composition
- oxygen composition
- temperature



- different type of disordering



- diffraction effects of nanostructuring



[Takeda Y. et al. // J. Solid State Chem. 1986. 63. 237.]

Weakly oxygen deficient $SrFeO_{3-\delta}$

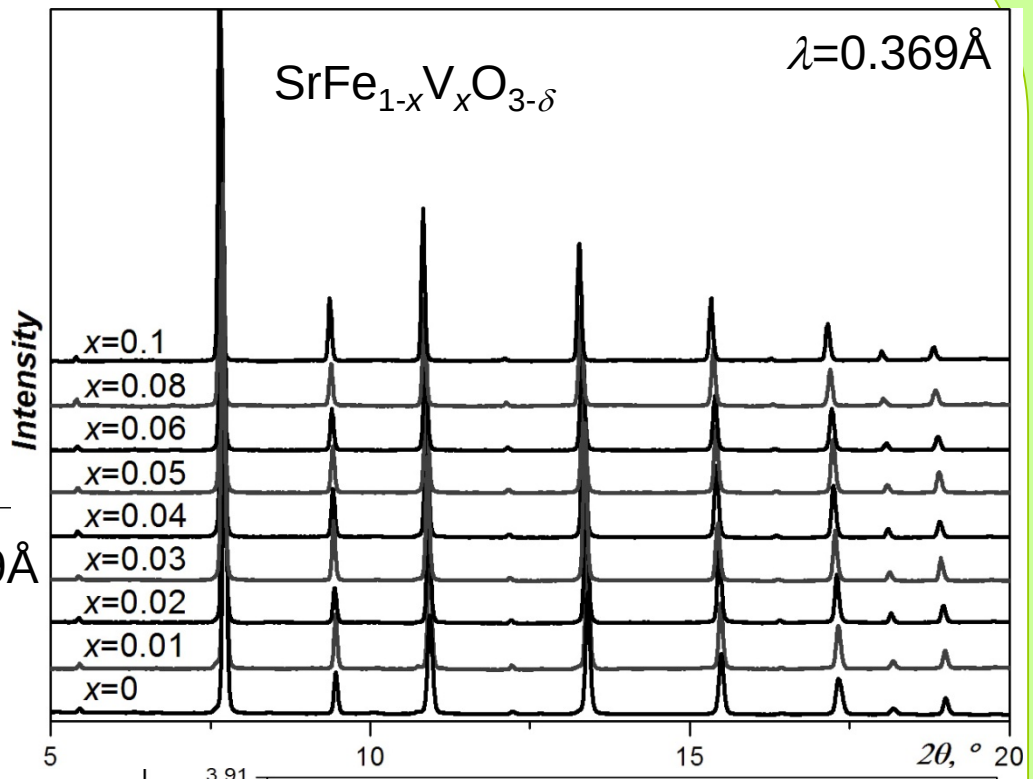
Slow cooling at air

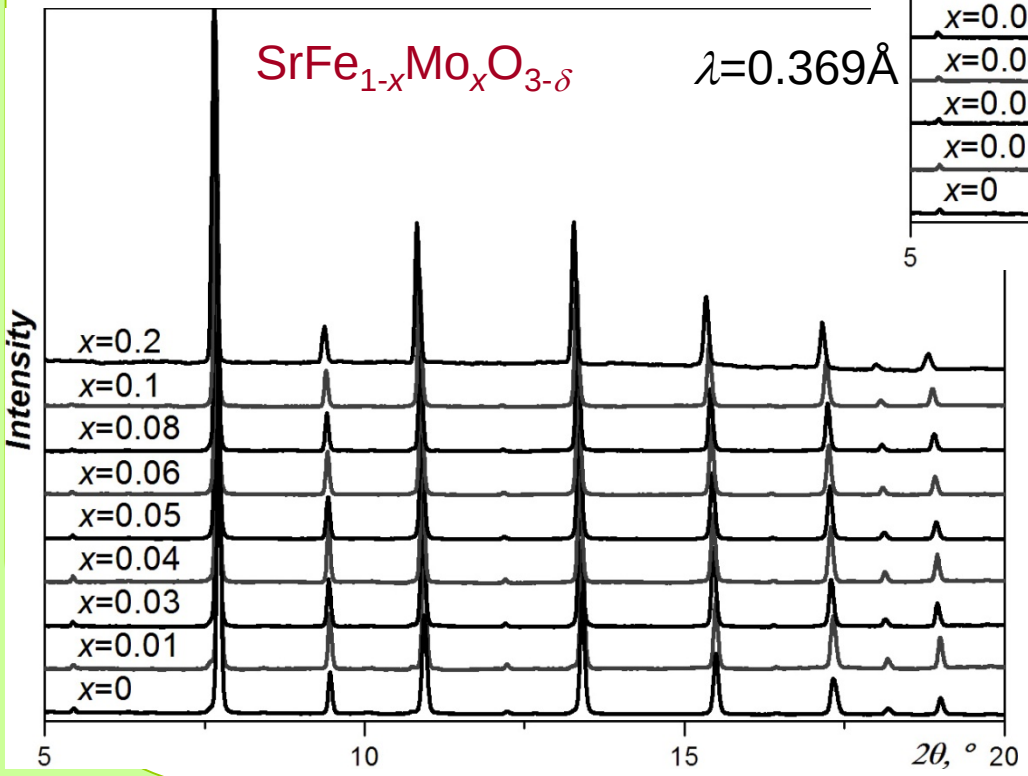
$3-\delta \approx 2.8-2.9$

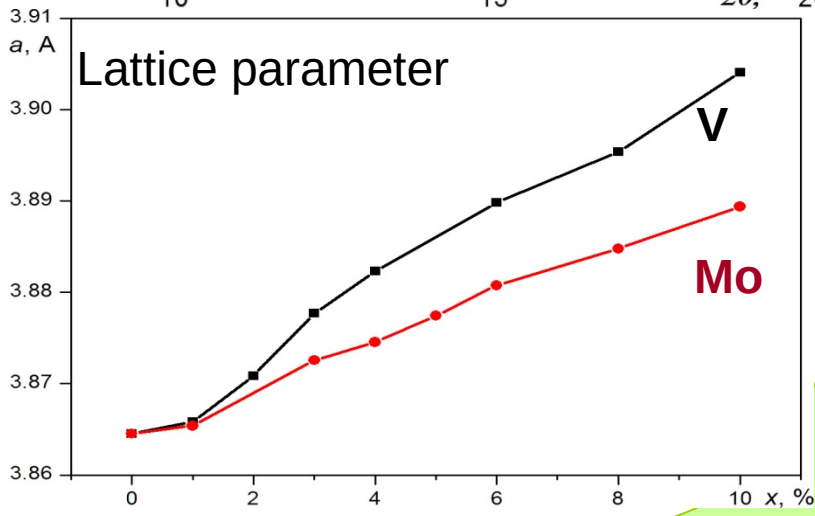
Substitution with high charged cations:

at normal conditions pO_2

cubic perovskite structure remains







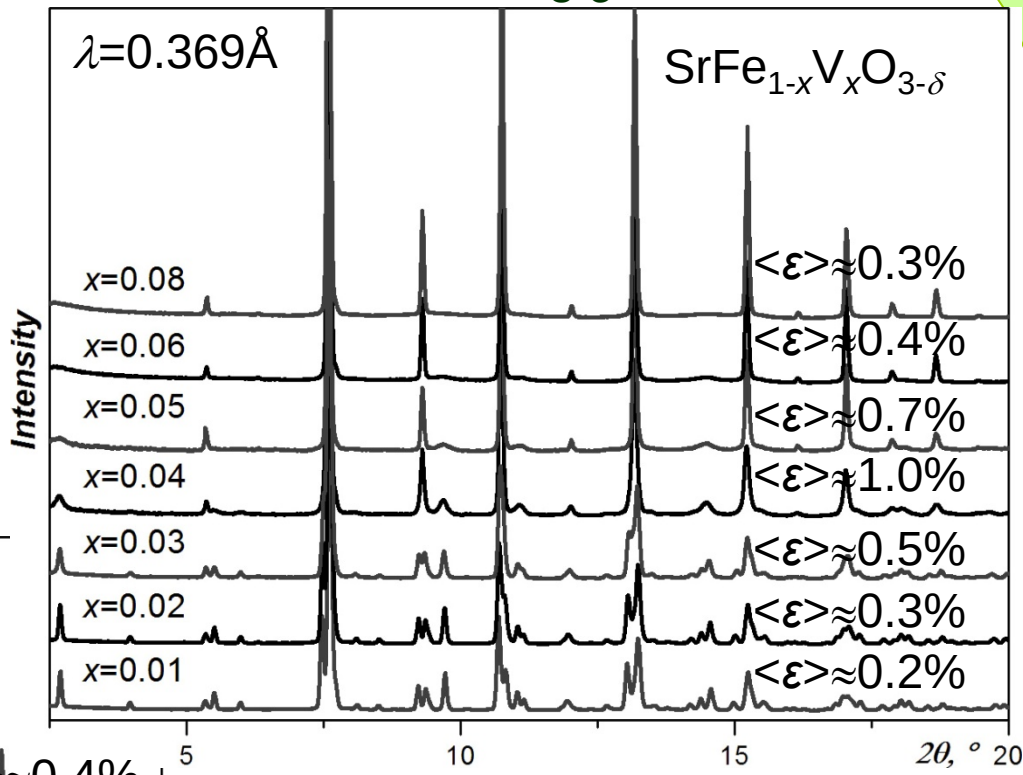
Strongly oxygen deficient $SrFeO_{3-\delta}$

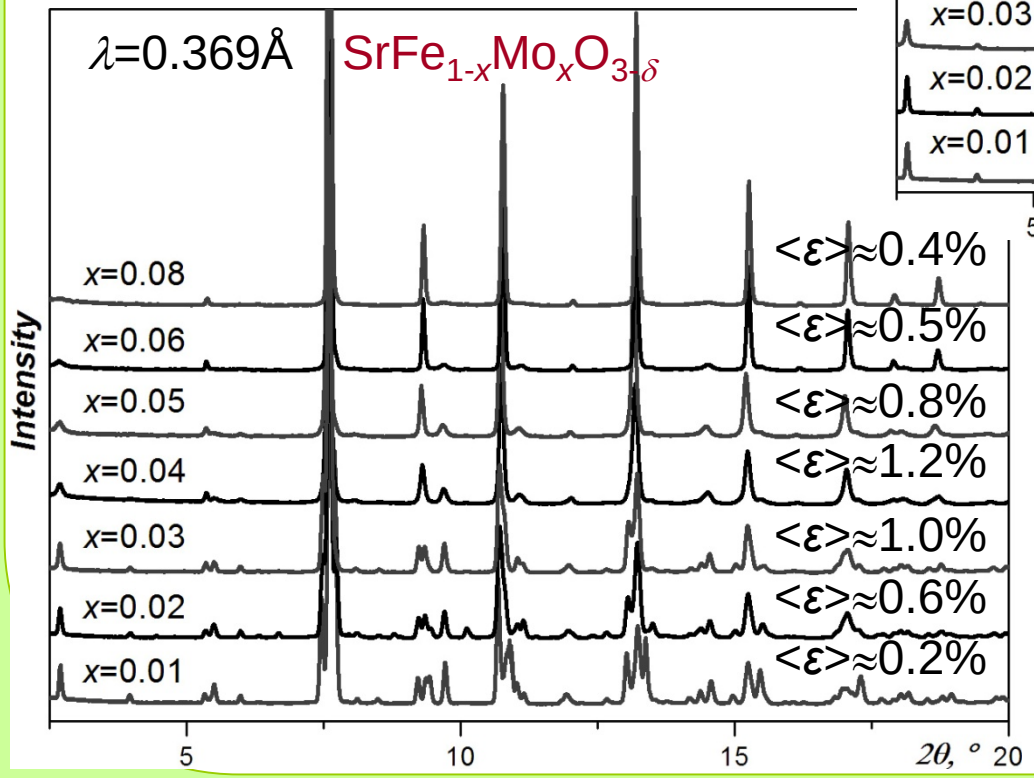
Quenching in vacuum

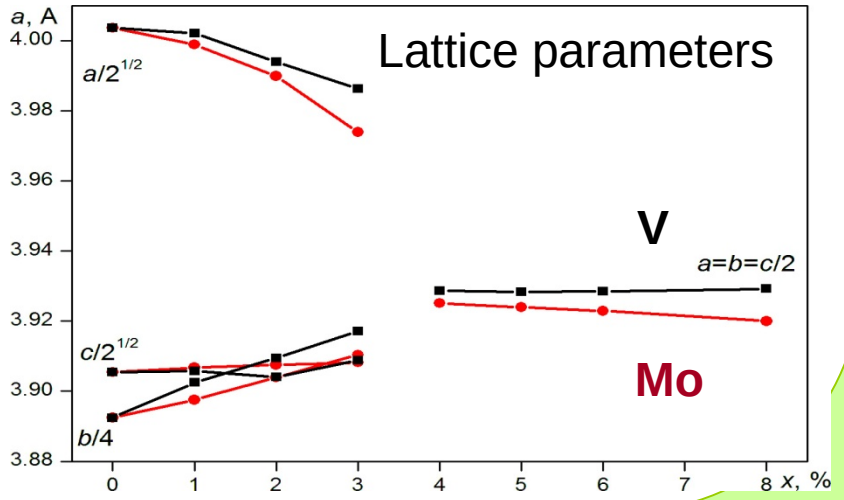
$3-\delta \approx 2.5-2.7$

Substitution with high charged cations:

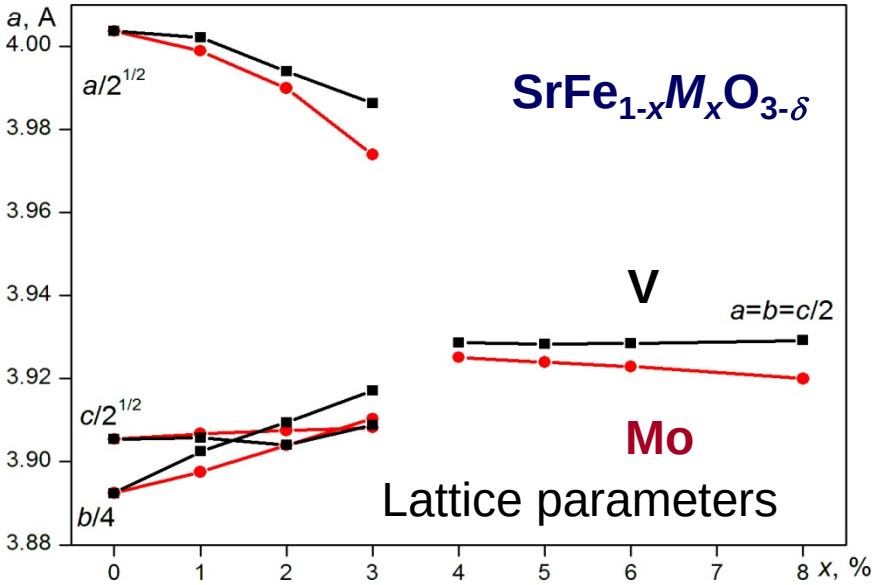
during quenching at low pO_2 cubic perovskite structure is not preserved

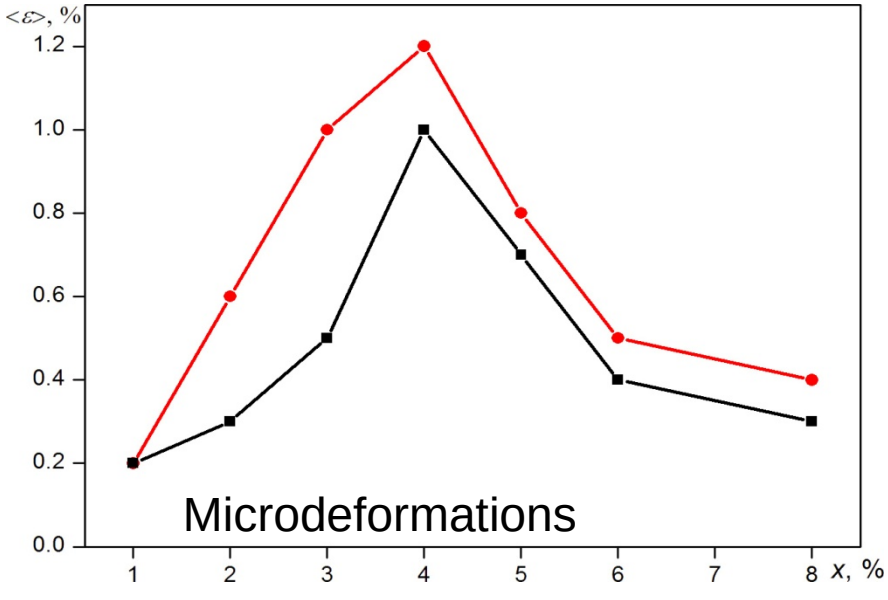


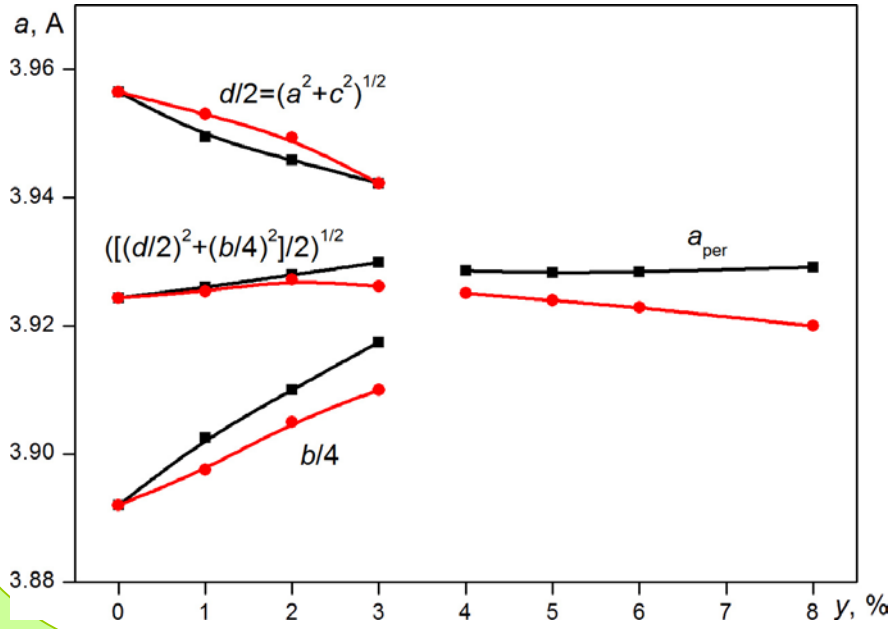




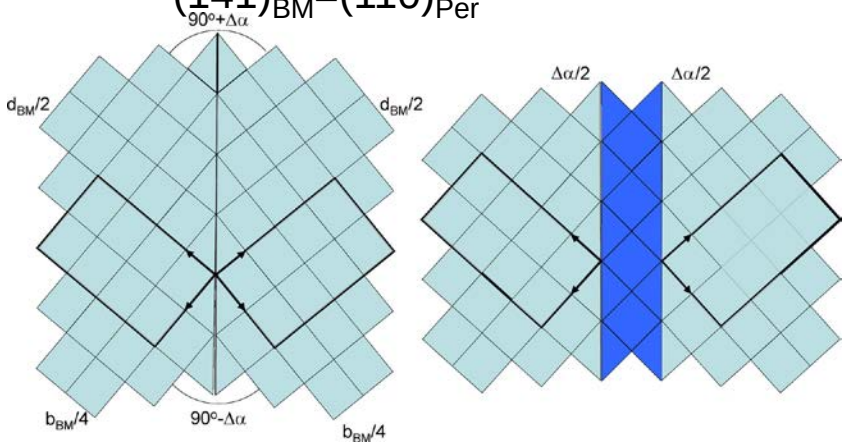
Strongly oxygen deficient $SrFeO_{3-\delta}$







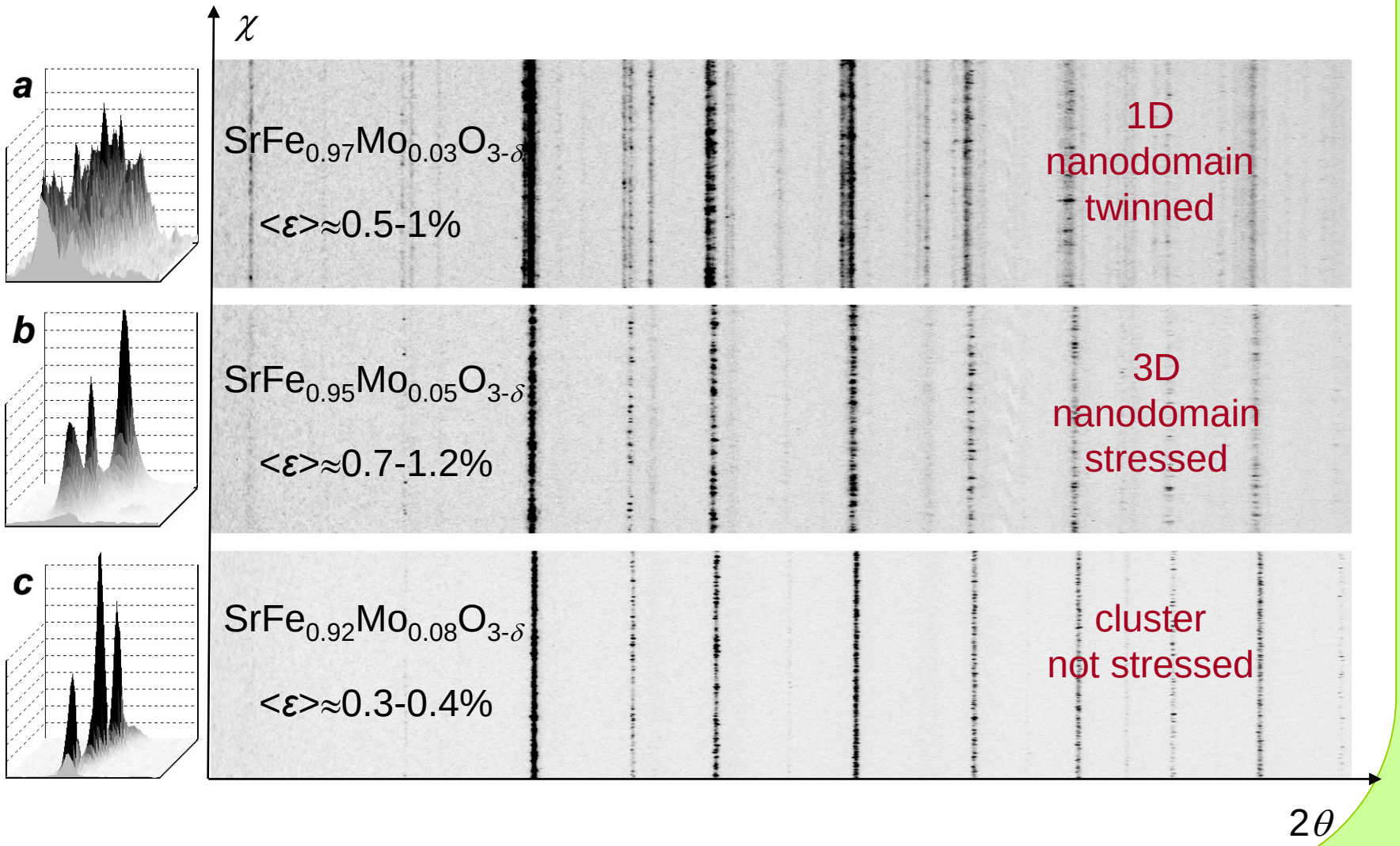
$(\underline{141})_{BM}=(110)_{Per}$



The reduced length of the unit cell along $(141)_{BM}$ plane $l = \sqrt{((b_{BM}/4)^2 + (d_{BM}/2)^2)/2}$ almost does not change, which means that twinning direction is the least stressful in *bd* plane.

Strongly oxygen deficient $SrFeO_{3-\delta}$

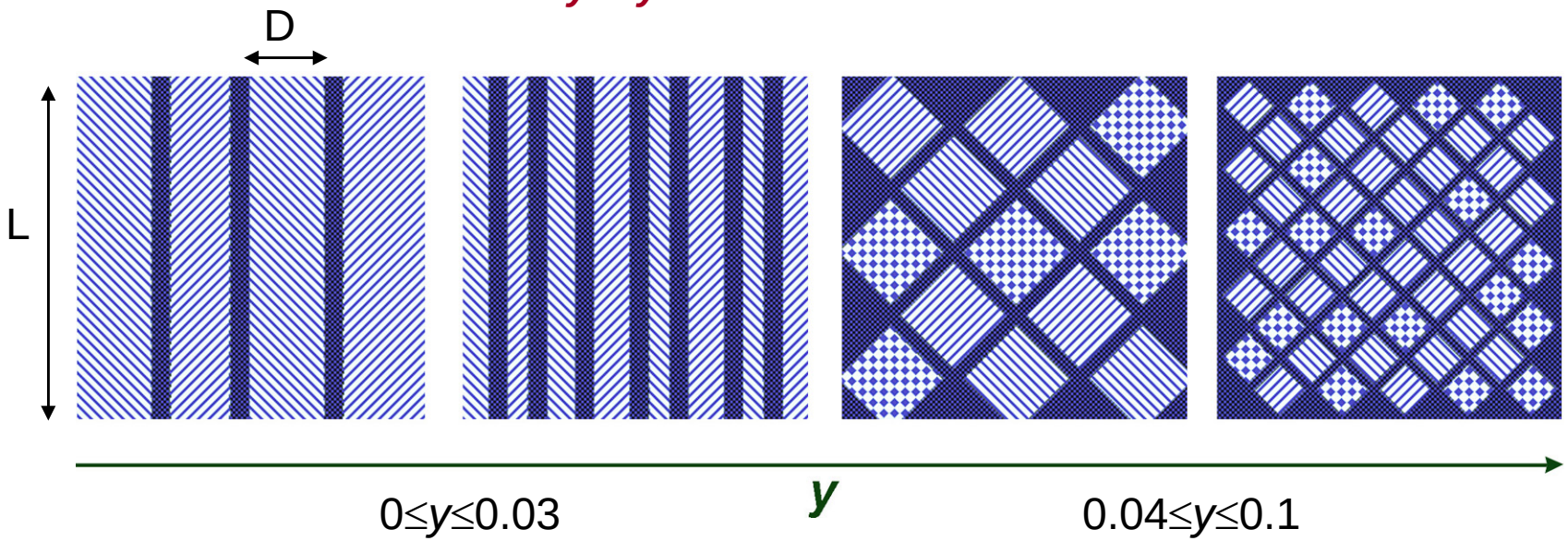
2D- diffraction $I(2\theta, \chi)$



Strongly oxygen deficient $SrFeO_{3-\delta}$

Nanodomain states according to HRTEM

$SrFe_{1-y}M_yO_{2.5+x}$ (M=V,Mo)



$\langle L\rangle_{min}=\langle D\rangle_{max} \approx$ 20-40nm; $\langle D\rangle_{min} \approx$ 2-5nm

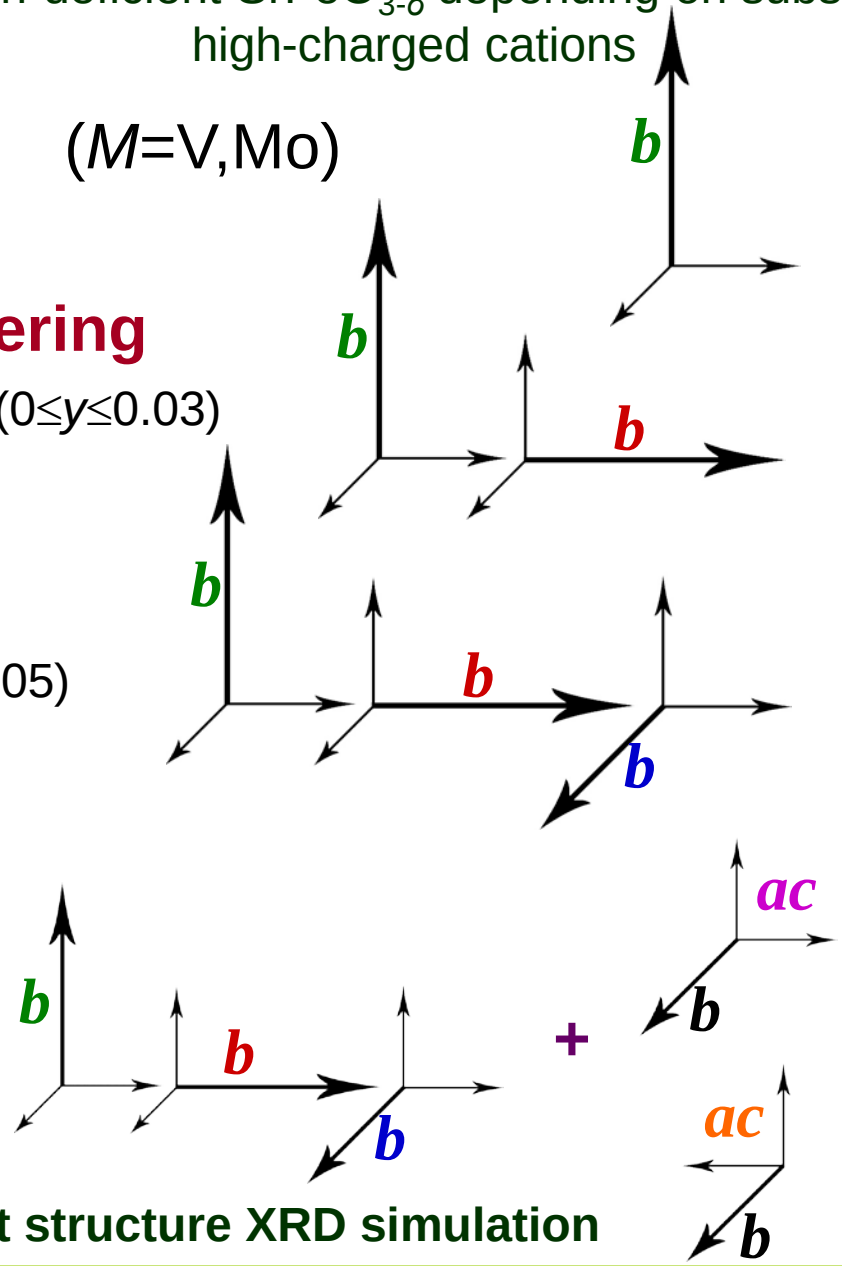
Nanodomain states

Of strongly oxygen-deficient $SrFeO_{3-\delta}$ depending on substitution degree of high-charged cations

$SrFe_{1-y}M_yO_{2.5+x}$ (M=V,Mo)

Increase in degree of disordering in the system

y



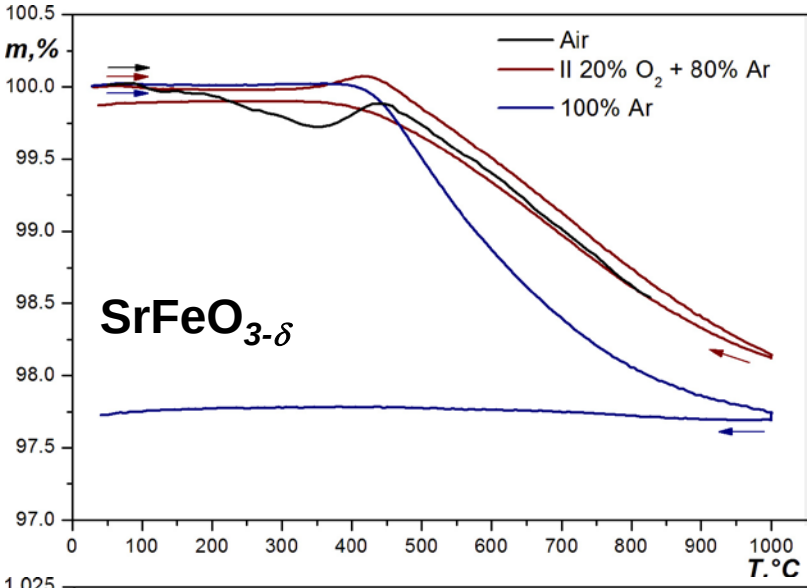
states:

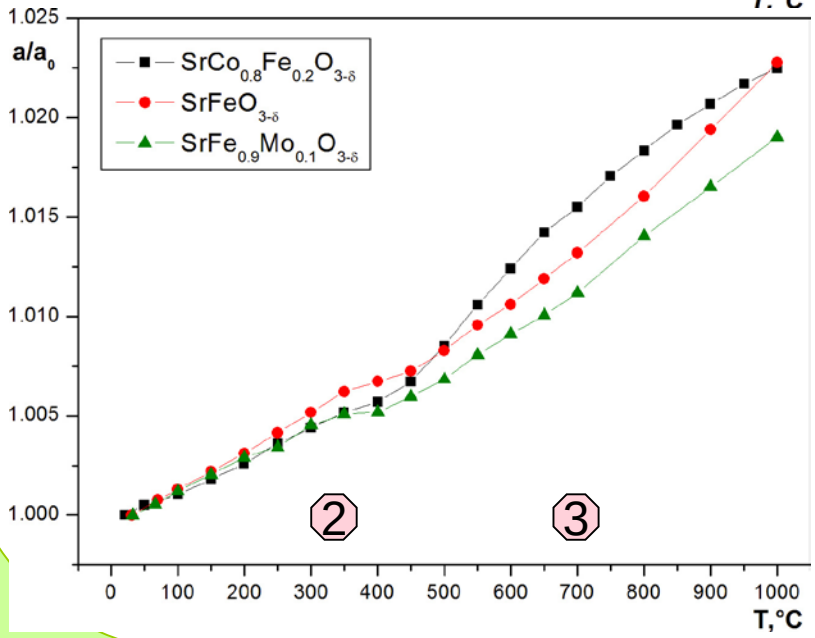
monodomain	1
1D nanodomain twinned	2
3D nanodomain stressed	3
cluster not stressed	12 (6)

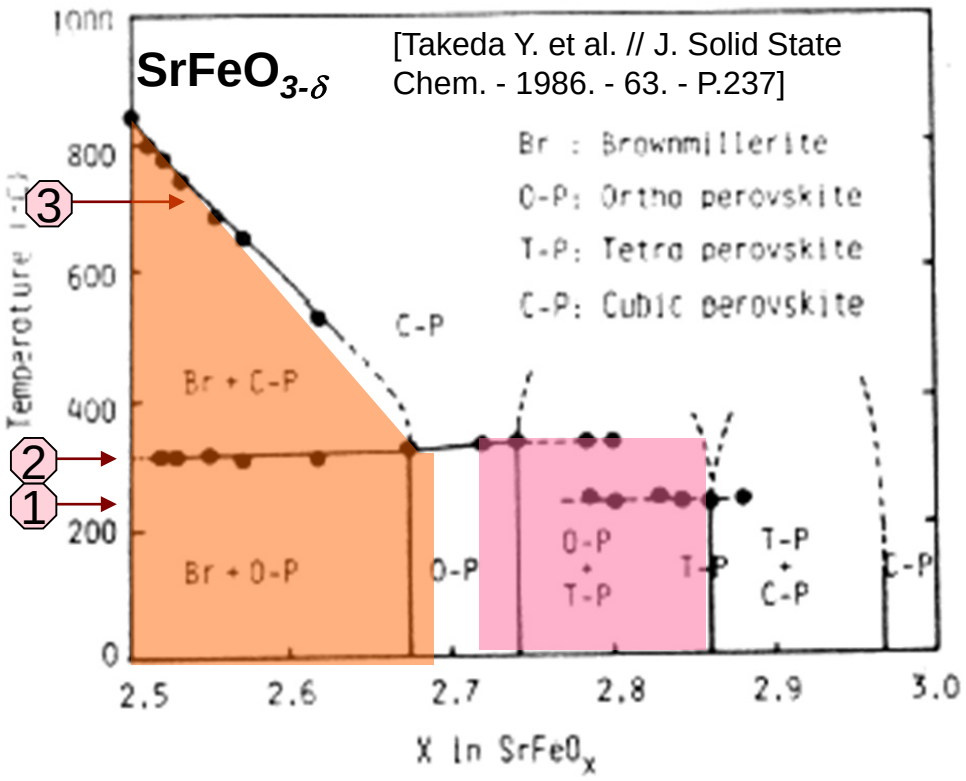
according to defect structure XRD simulation

Structure changes at heating to high temperatures

Phase transitions of vacancy-ordered phases







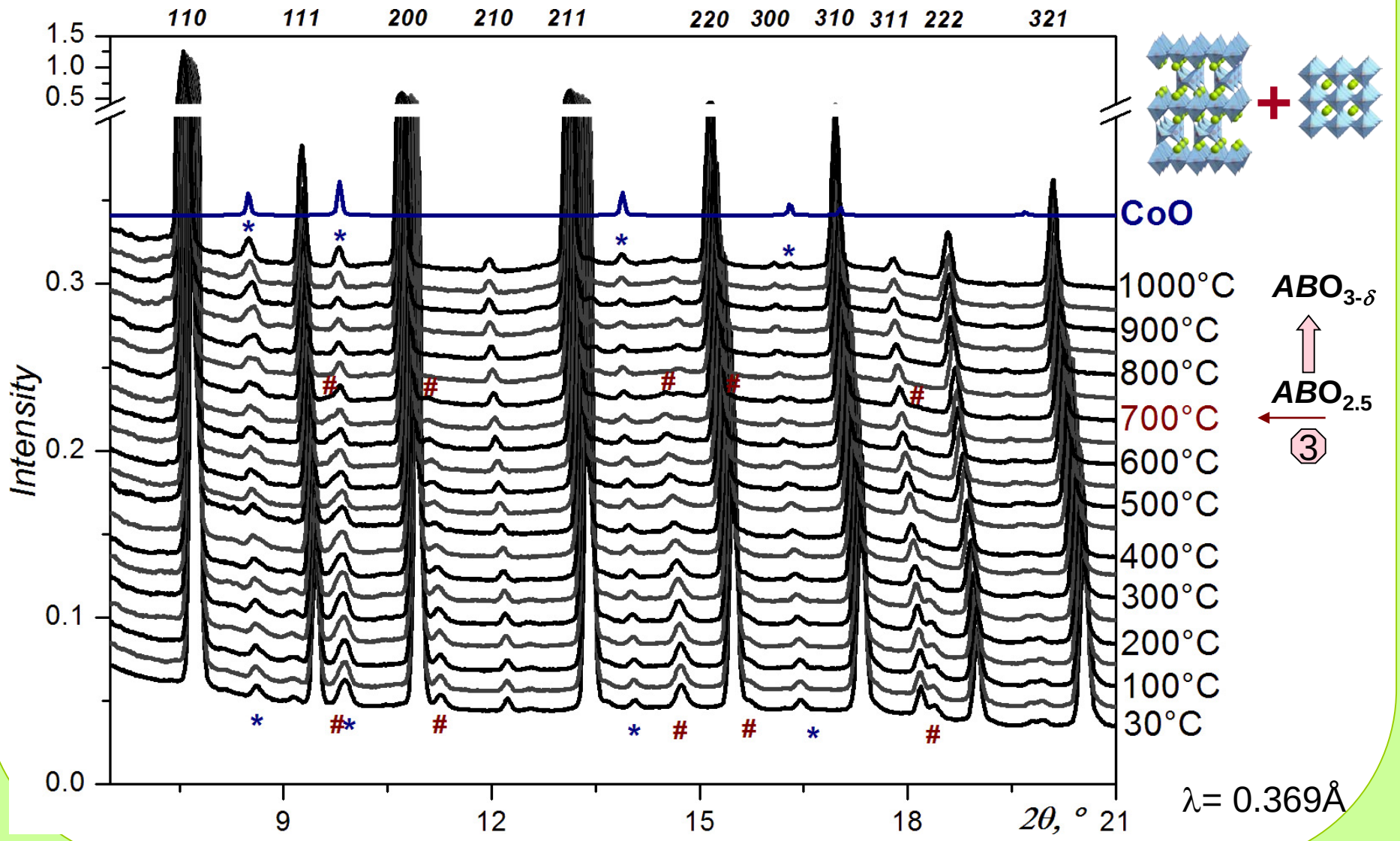
ООПООП' $ABO_{2.875}$ ↓ ① $ABO_{3-\delta}$

ОПОП' $ABO_{2.75}$ ↓ ② $ABO_{3-\delta}$

ОТОТ' $ABO_{2.5}$ ↓ ③ $ABO_{3-\delta}$

Structure changes at heating to high temperatures

Evolution of superstructural reflections $SrCo_{0.8}Fe_{0.2}O_{2.5+x}$ $x \approx 0.14$

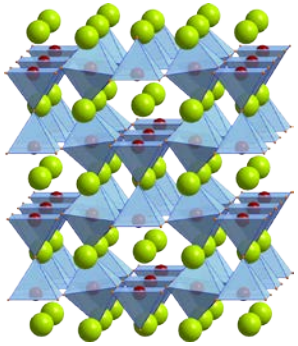


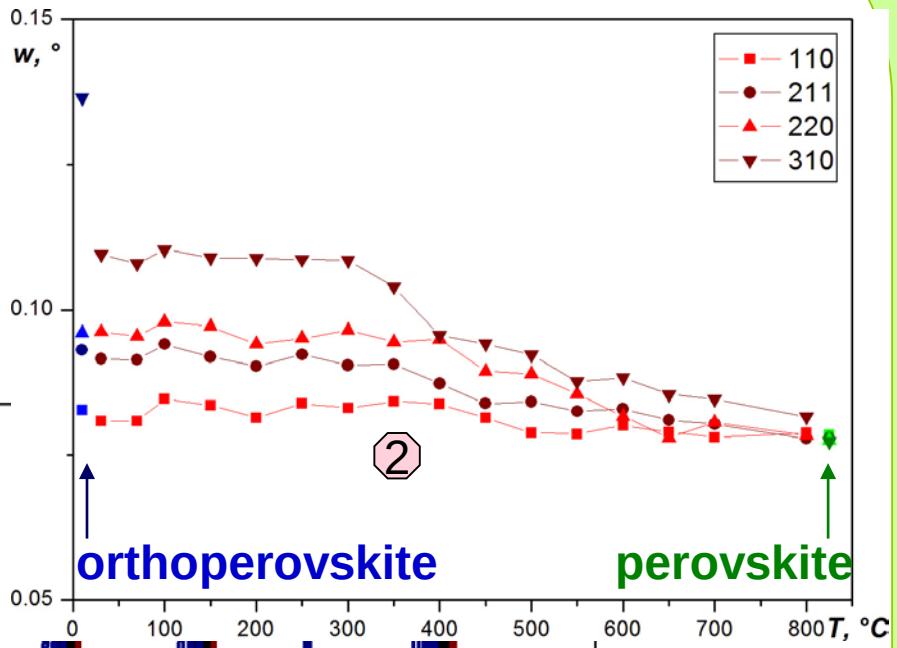
Structure changes at heating to high temperatures

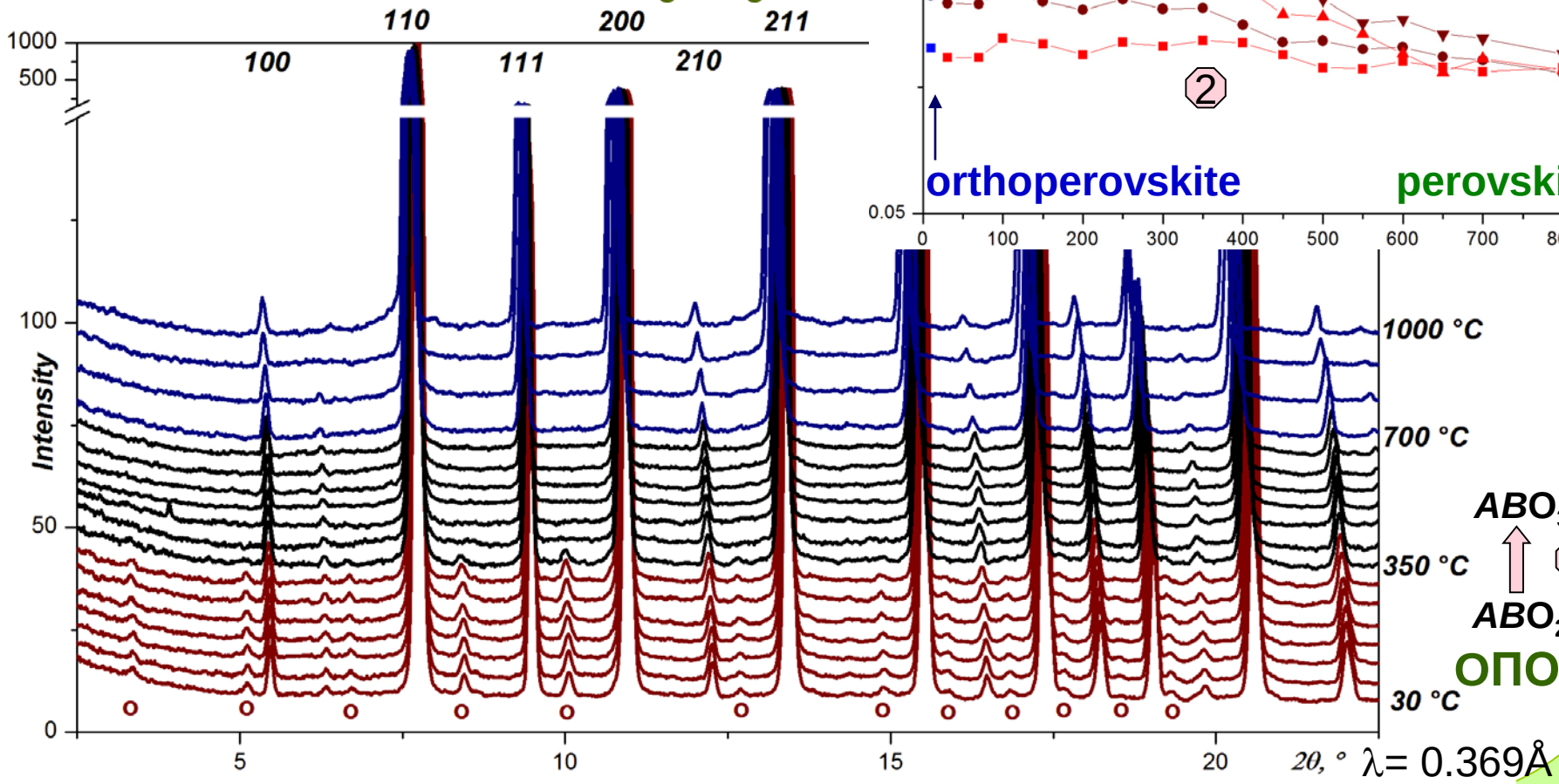
Nanodomain states of orthoperovskite

$SrFeO_{2.75+x}$ $x \approx 0.07$

$$\frac{a}{2\sqrt{2}} \neq a_{per}; \frac{b}{2} \neq a_{per}; \frac{c}{\sqrt{2}} \neq a_{per}$$







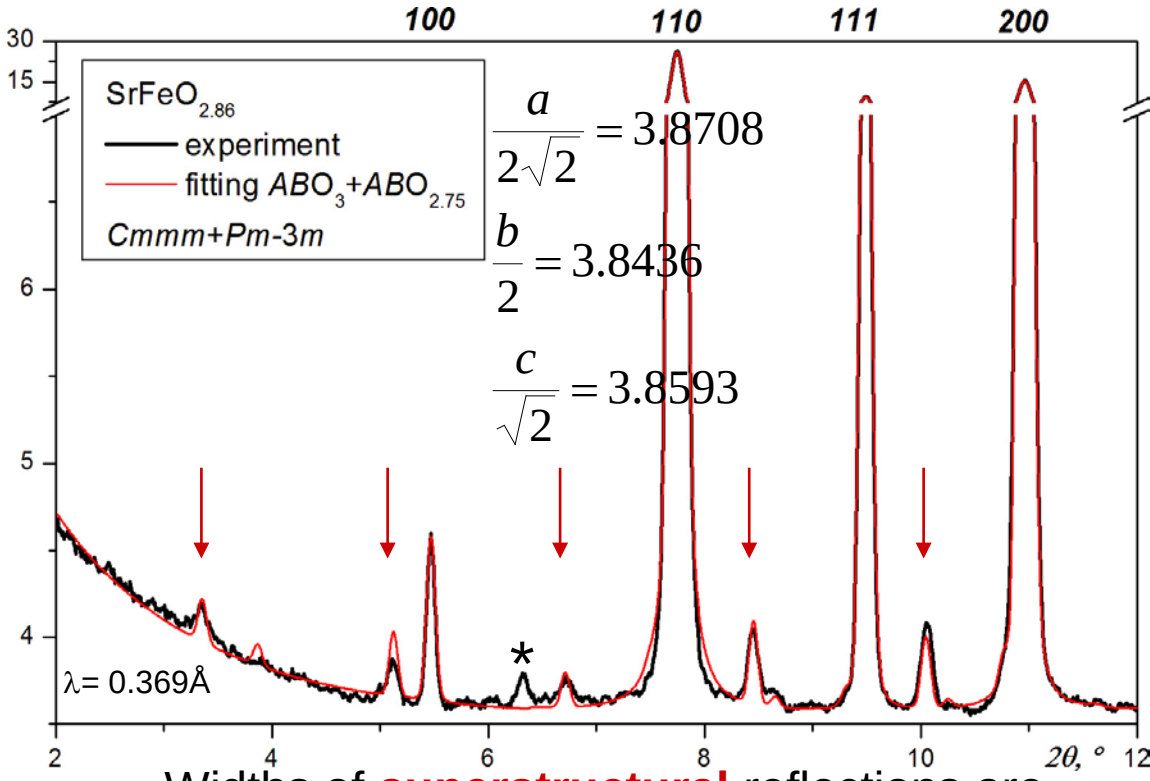
$ABO_{3-\delta}$ ② $ABO_{2.75}$

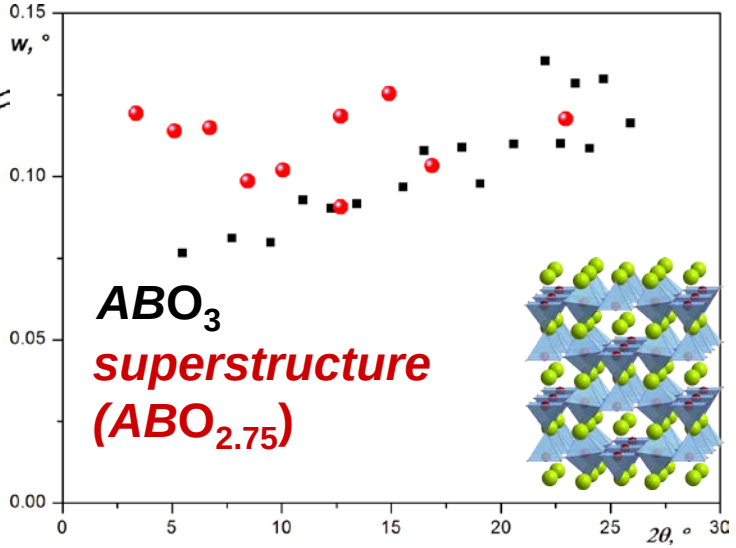
ОПОП'

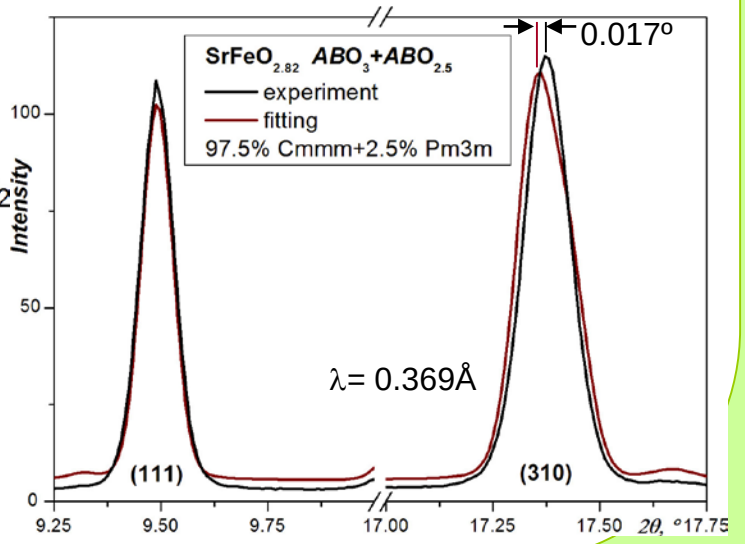
Domain structure of orthoperovskite

Influence on XRD

$SrFeO_{2.82}$



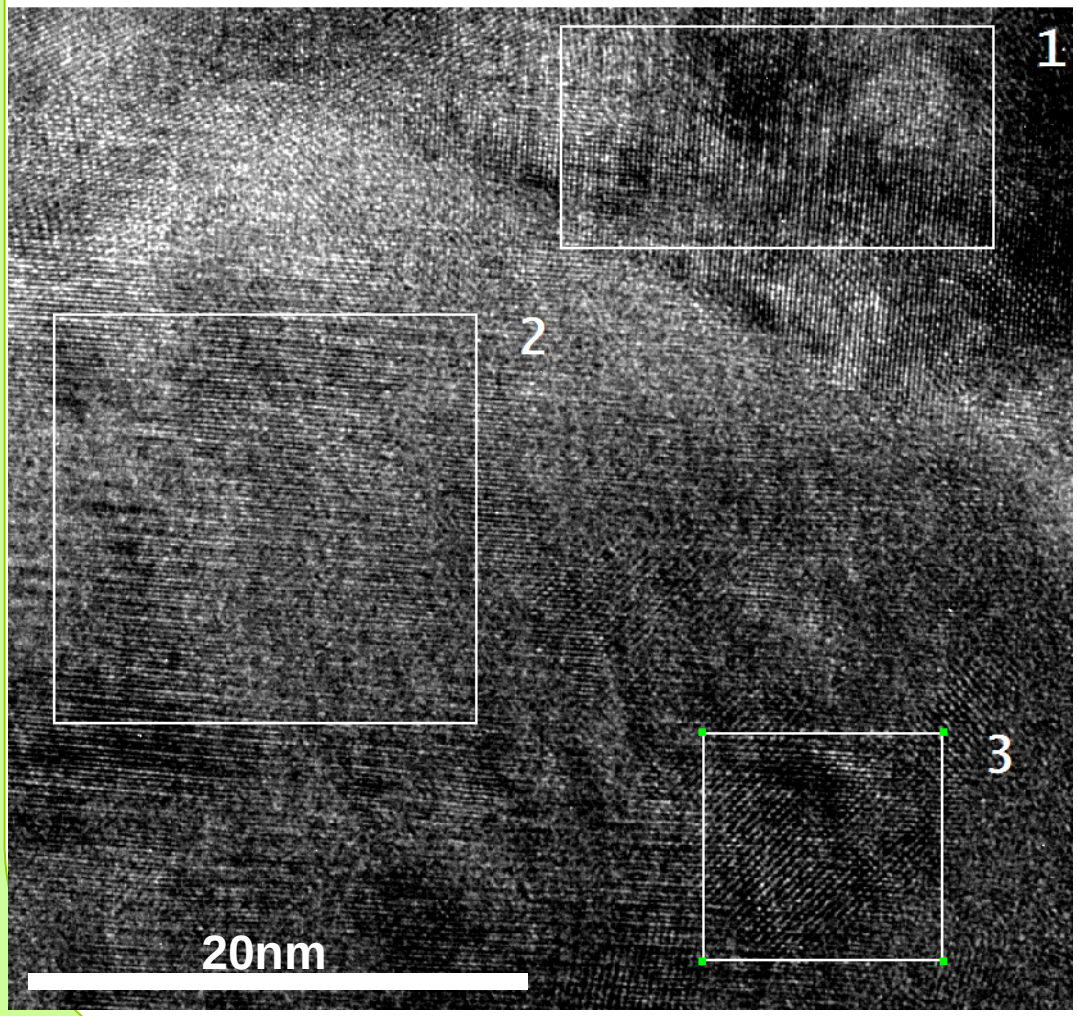


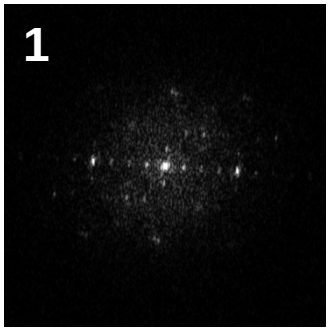


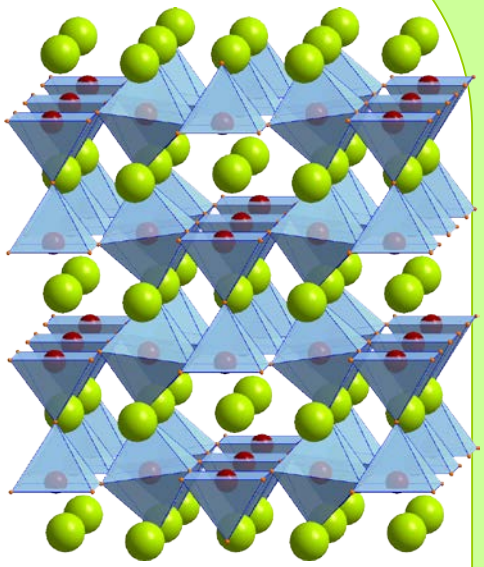
- Widths of **superstructural** reflections are higher then for **main**
- Forms of peaks are symmetrical in despite of low symmetry of orthoperovskite

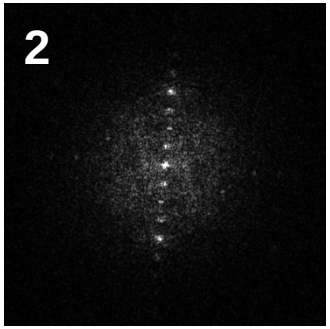
Domain structure of orthoperovskite at HRTEM

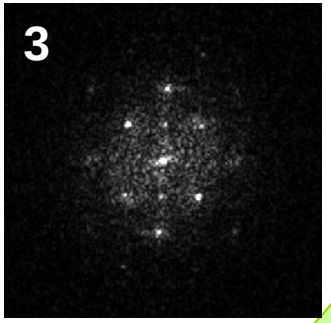
$SrFeO_{2.82}$ obtained by slow cooling in air





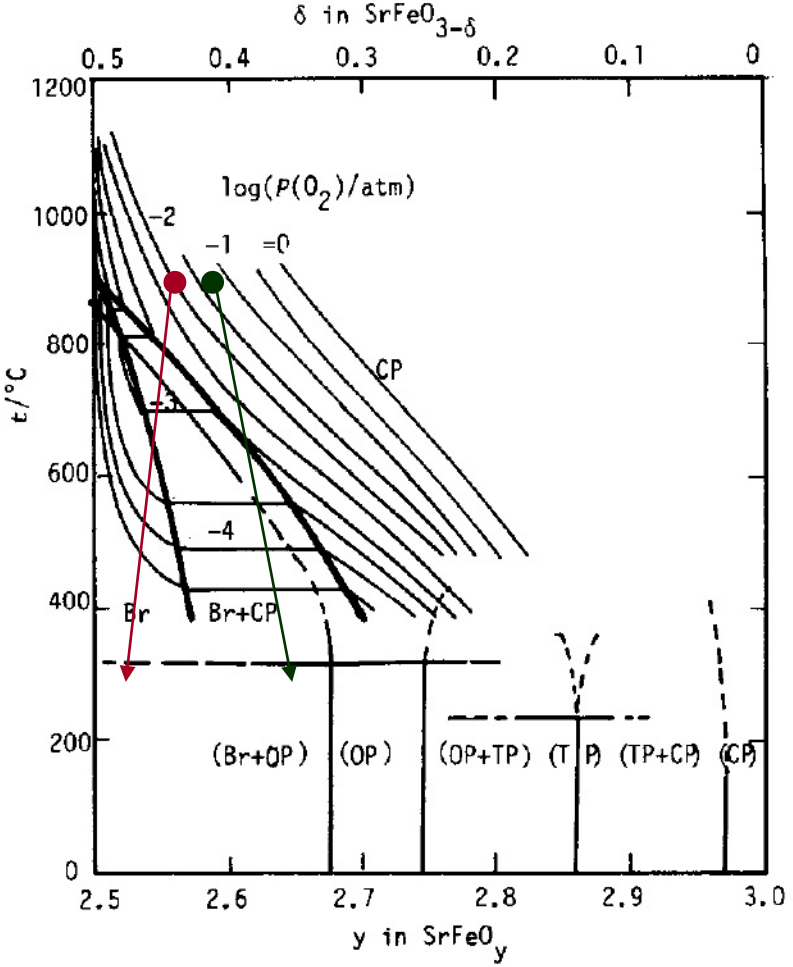




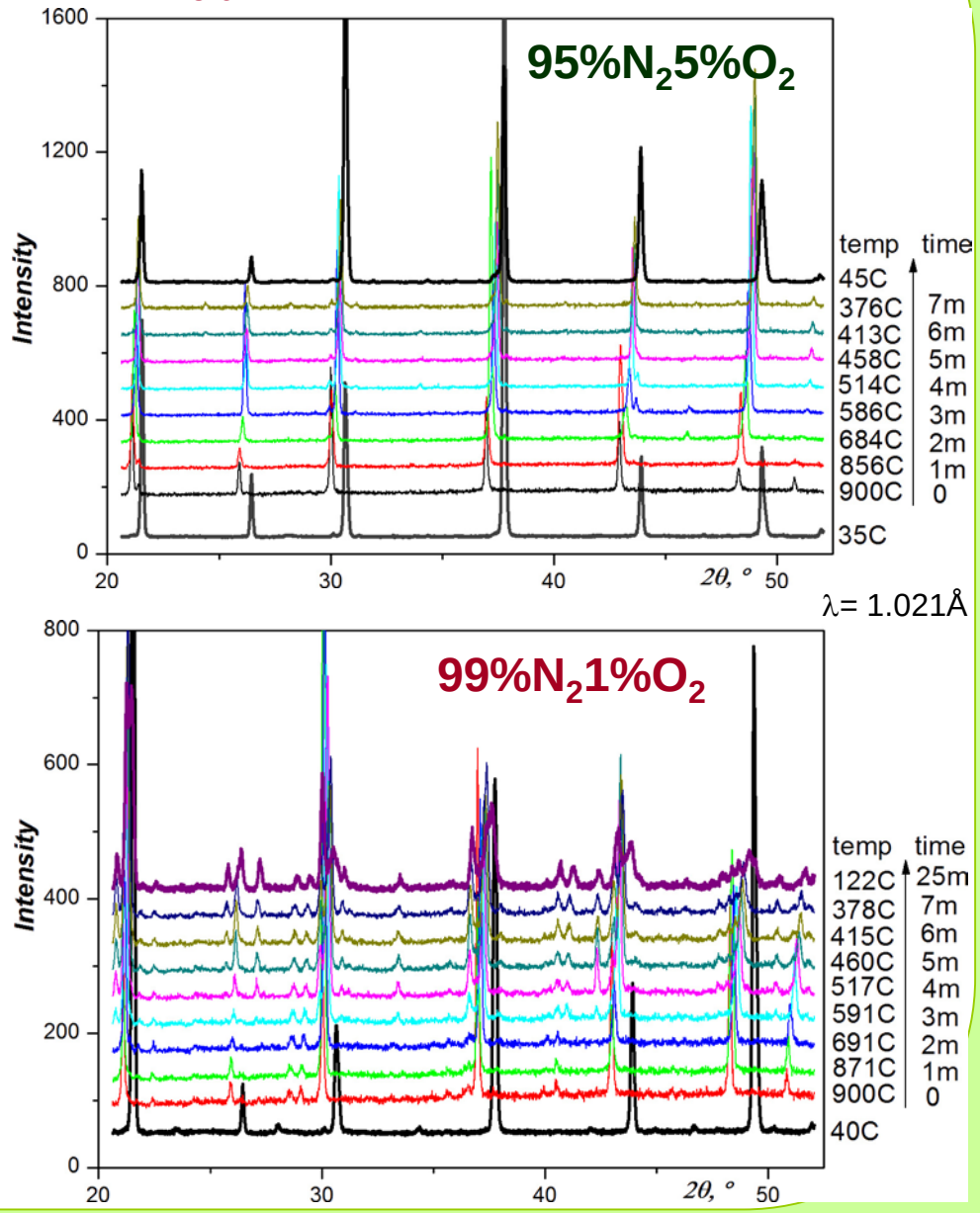


Structure changes at heating to high temperatures

In situ XRD investigations of quenching $SrFeO_{3-\delta}$ in oxygen-deficient atmosphere



[Mizusaki J. et al. // J. Solid State Chem. 1992. 99. 166.]



Thank you very much for your attention!