Hopping and clustering of oxygen vacancies in $BaTiO_{3-\delta}$ and the influence of the dynamically disordered off-centred Ti atoms

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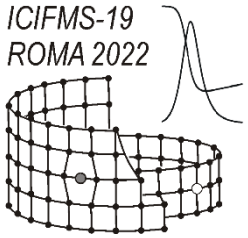
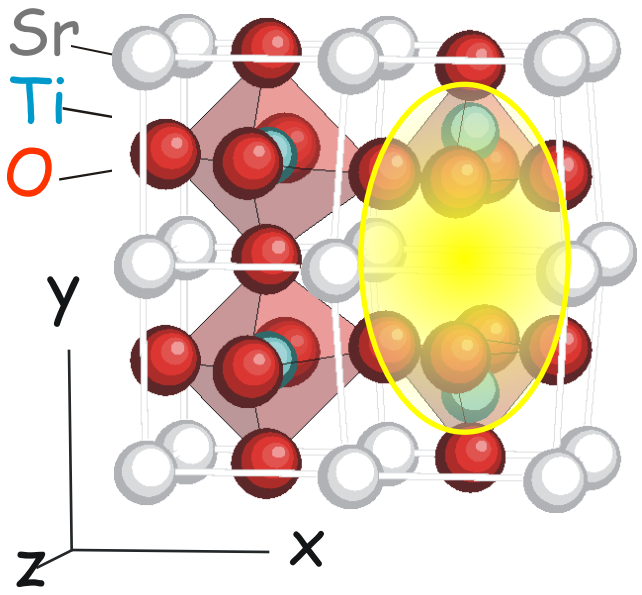


ICIFMS-19 (Rome, 2022)

Summary

- brief introduction on O vacancies in perovskites
- anelastic spectra of $SrTiO_{3-\delta}$: free, paired and aggregated V_O
- anelastic spectra of $BaTiO_{3-\delta}$: similar but
- the barrier for the hopping of an isolated V_O is larger and decreases with increasing δ
- the anisotropy of the elastic dipole is three times larger
- simple explanation in terms of Ti dynamically off-centred over 8 positions also in the cubic phase

Perovskite cubic structure and O vacancies



formula: ABX_3, e.g. $SrTiO_3$

high T: cubic structure;

low T: distortions and rotations of the O octahedra and cation off-centering

variety of properties: ferroeletricity, giant magnetoresistance, ionic conductivity, superconductivity

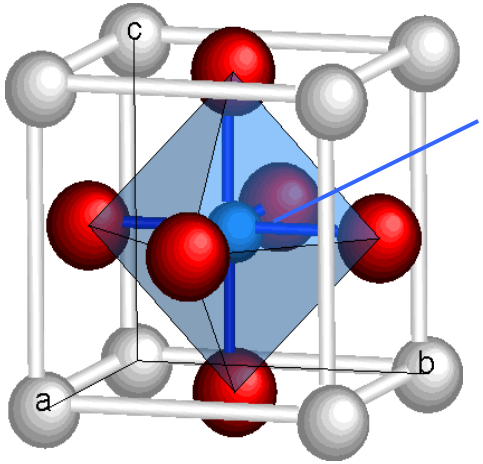
O vacancy in undoped cubic perovskite:

only elastic dipole → anelastic but not dielectric relaxation

$$\lambda^{(v)} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_1 \end{pmatrix}$$

$$\Delta\lambda = \lambda_2 - \lambda_1$$

Defects and compensating O vacancies



Sr/Ba^{2+}

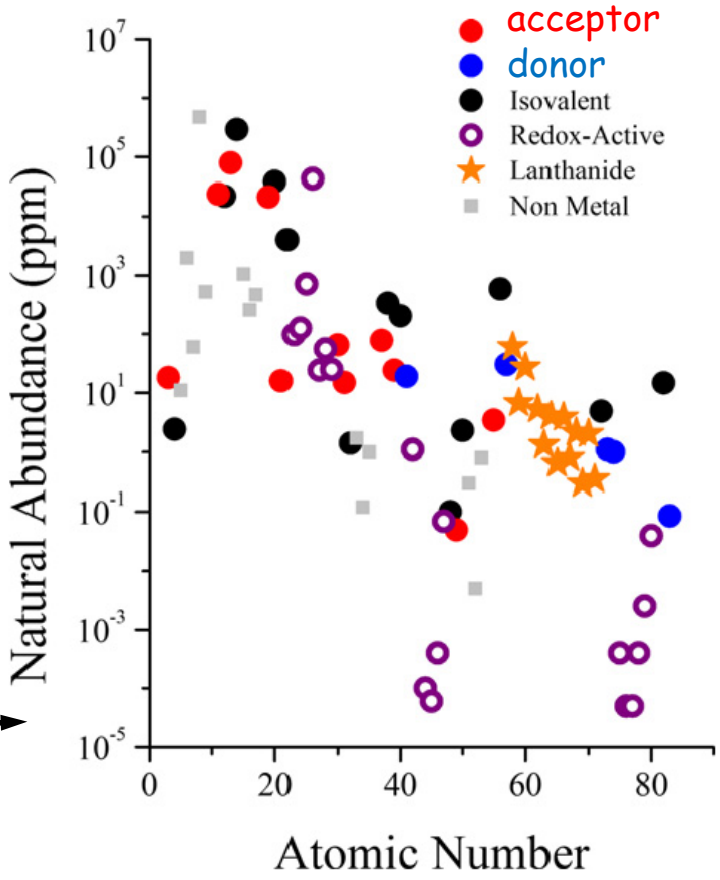
Ti^{4+}

O^{2-}

in a purely ionic picture the defects are charge compensated:

$V_{Ba}^{2-} + V_O^{2+}$ cation vacancy

$(2\ K^{+}_{Ba})^{2-} + V_O^{2+}$ acceptor impurity (more abundant than donors)



Maier and Randall
J. Am. Ceram. Soc.,99 3360 (2016)

the ionic picture is a schematization:

- the bonds are partially covalent
- V_O may have charge 2+, 1+, 0

V_O may be introduced in a stoichiometric material by heating in an O free or reducing atmosphere (***CO*** + O → CO_2 + V_O or $\mathbf{H_2}$ + O → H_2O + V_O)

sample surface — goes into the bulk

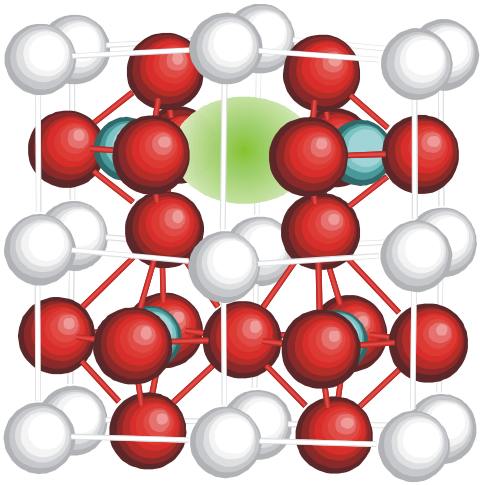
Importance of O vacancies in perovskites

Ionic conductors (e.g. $BaCe_{1-x}Y_xO_{3-x/2}$): V_O and H are the charge carriers

High-T_C superconductors (e.g. $YBa_2Cu_3O_{7-x}$): doping depends on the concentration and ordering of O in non-stoichiometric planes

ferroelectrics (e.g. $PbZr_{1-x}Ti_xO_3$): V_O are considered responsible for aging and fatigue

Elastic dipole of an O vacancy (calculations)



Calculations of atomic displacements around V_O

C.H. Park and D.J. Chadi, Phys. Rev. B **57**, R13961 (1998)

small outward shifts of nn Pb and Ti and inward shifts of nn O (electrostatic interaction)

Buban *et al.*, PRB **69**, 180102 (2004)

larger and longer range atomic displacements with larger supercell size

The elastic dipole of an O vacancy in a perfect perovskite lattice might be very small and nearly isotropic

D. A. Freedman et al., Phys. Rev. B 80, 064108 (2009)

F. Cordero
PRB 76, 172106 (2007)

V_O^{2+} in $SrTiO_3$: $Tr(\lambda) = 0.0039$ $\Delta\lambda = 0.41$ (= 18 $\Delta\lambda_{mea}$)

E.J. Granhed *et al.*, J. Mater. Chem. A 7, 16211 (2019)

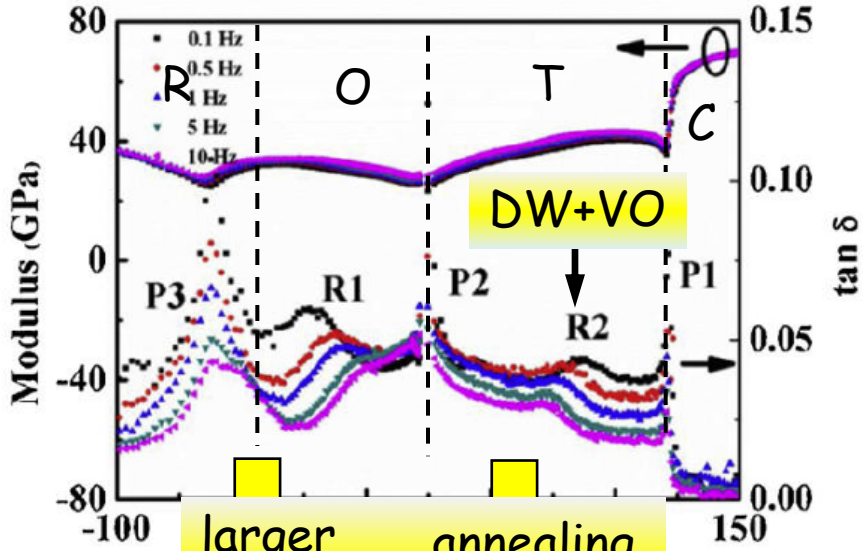
anelastic relaxation

V_O^{x} in $BaTiO_{3-x}H_x$: $Tr(\lambda) = -0.049$ $\Delta\lambda = 0.067$ (= 0.87 $\Delta\lambda_{mea}$)

F. Cordero et al.
jalcom 874, 159753 (2021)

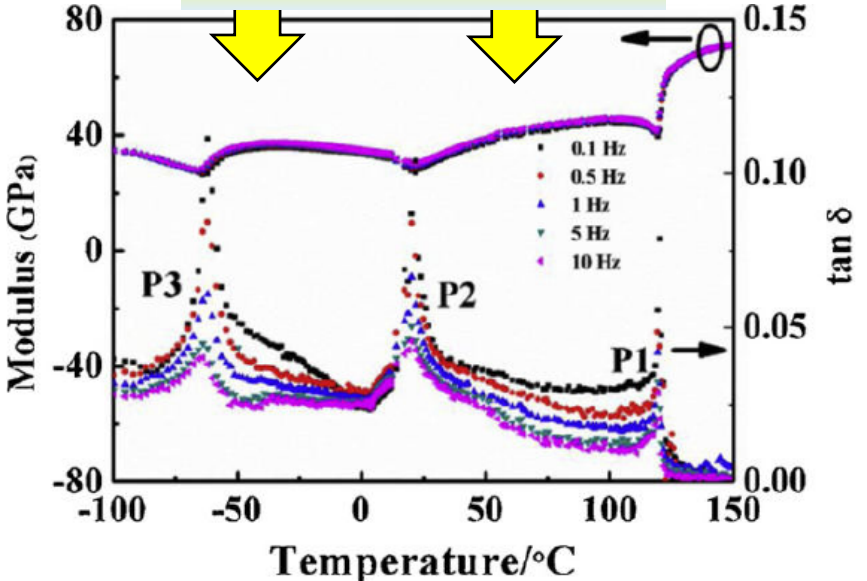
Ceramic $BaTiO_{3-\delta}$ - previous anelastic measurements

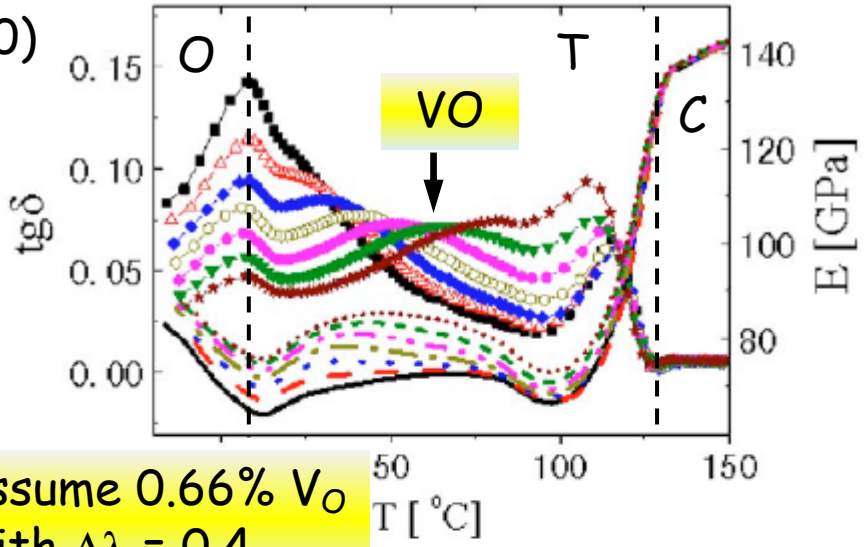
Y. Chen *et al.* J. Eur. Ceram. Soc. 40 391 (2020)



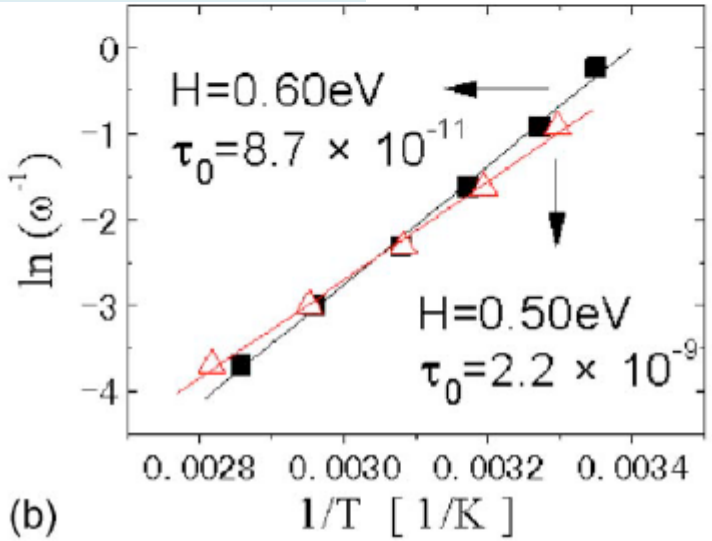
larger grains

annealing in O_2



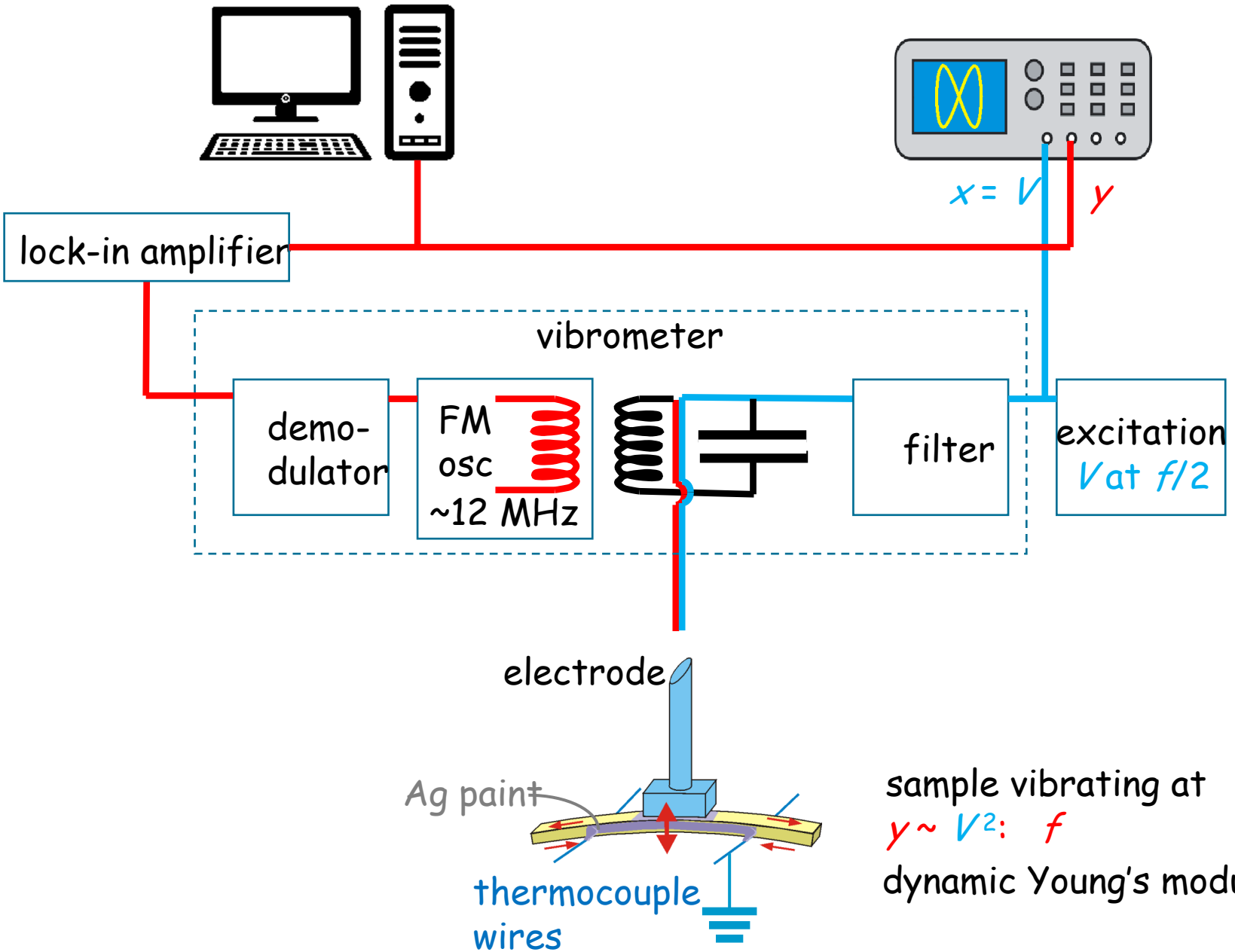


assume 0.66% V_O with $\Delta\lambda = 0.4$



. Chen *et al.* Appl. Phys. Lett. **89**, 071916 (2006)

Anelastic measurements - free flexural resonance



Experimental - samples

ceramic $BaTiO_3$

preparation in UFSCar, São Carlos

bar sintered at 1350 °C for 2 h

93.6% of the theoretical density

cut into two bars 42 × 6.3 × 0.68 mm^3

Young's modulus, 1st and 3d flexural modes (2.2 and 12 kHz)

F. Cordero, F. Trequattrini, D.A.B. Quiroga, P.S. Silva Jr.
J. Alloys and Compounds 874 159753 (2021) Special Issue ICIFMS-19

single crystal $SrTiO_3$

sample: bar 26×3.4×0.5 mm^3 from wafer of M.T.I. Corporation; edges || <100>

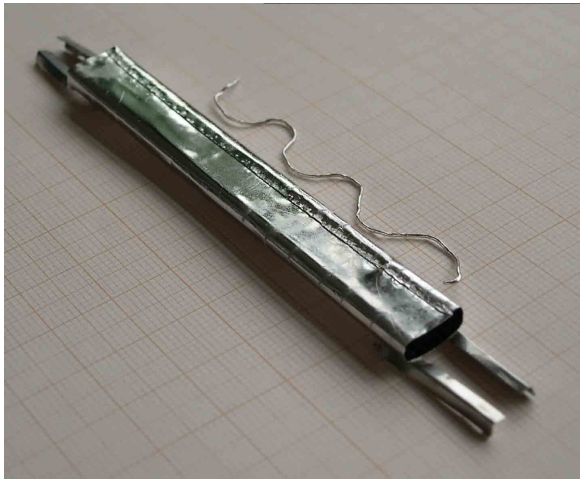
complex compliance s_{11}, 1st and 5th flexural modes (5.5 and 74 kHz)

F. Cordero, Phys. Rev. B 76, 172106 (2007)
F. Cordero, Mater. Sci. Engin. A 521-522 77 (2009) - ICIFMS-15

Experimental - sample reduction

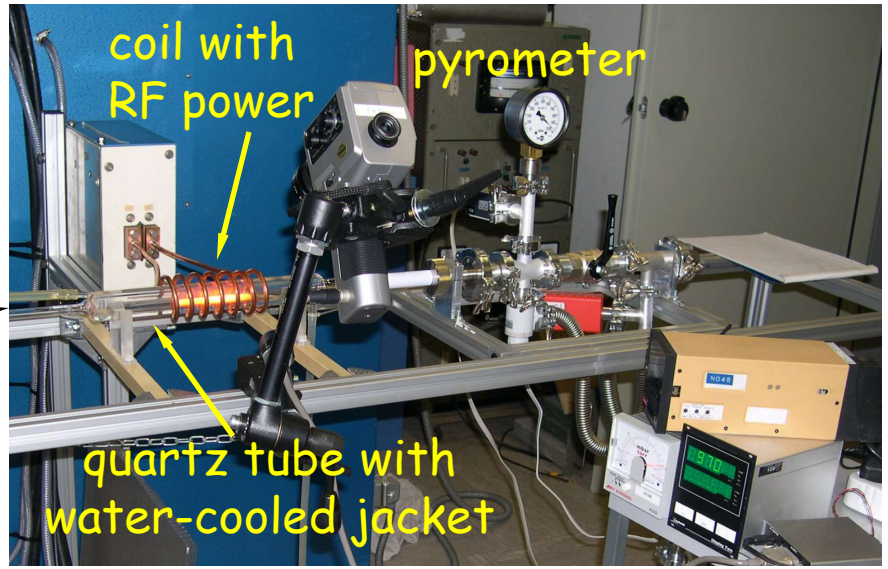
Induction heating at 900-1250 °C for 0.5-3 h in CO/O_2 flux
+ homogeneization 800 °C for 1 h

sample inserted in Pt holder



no anelastic relaxation peak appearing after reduction can be due to H

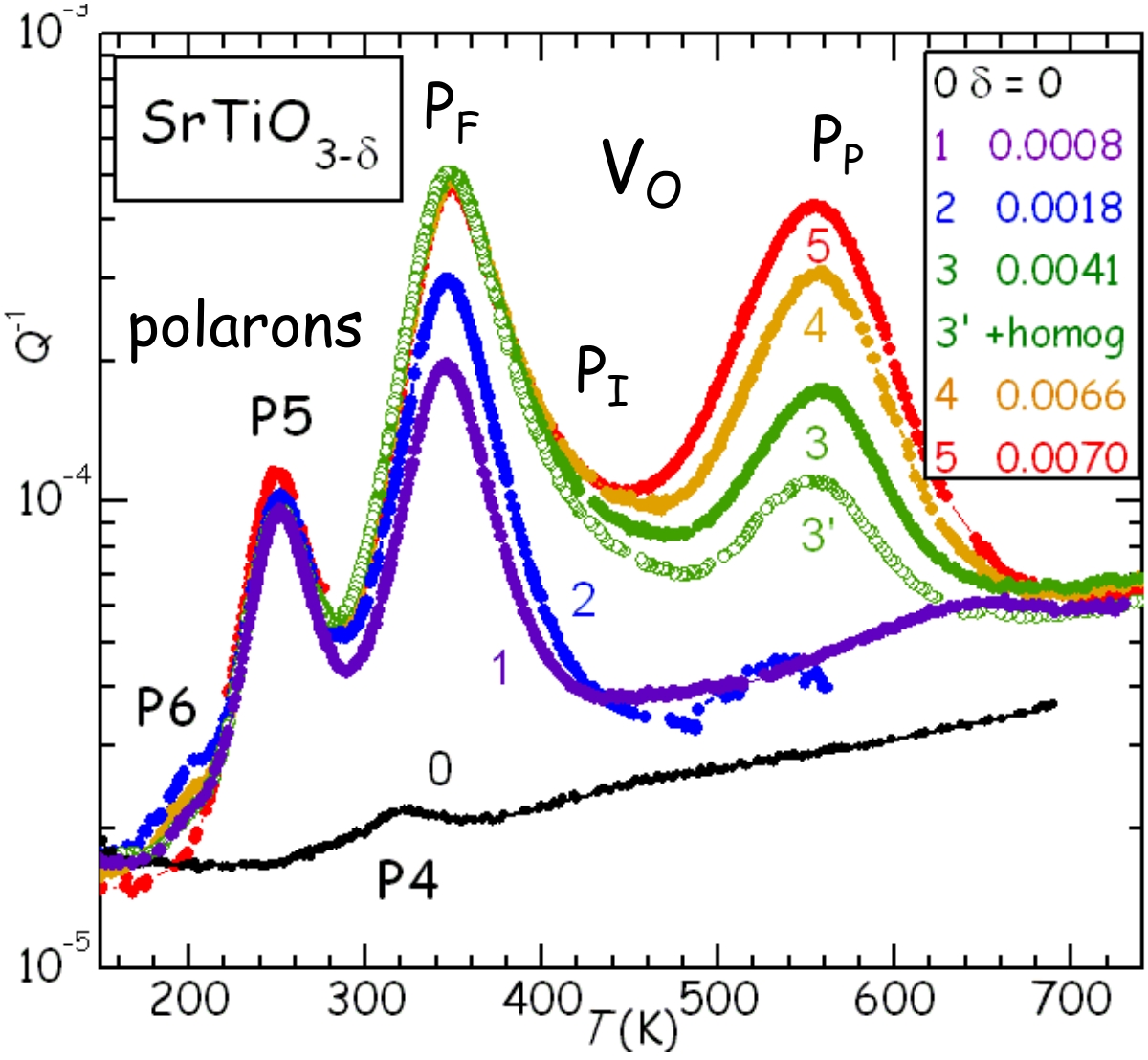
flow of ~1000 mbar
$0.1CO + 0.9Ar$ or O_2



O stoichiometry:

- mass change after reduction and reoxygenation
- temperature of the structural phase transition

Anelastic spectrum vs *x*



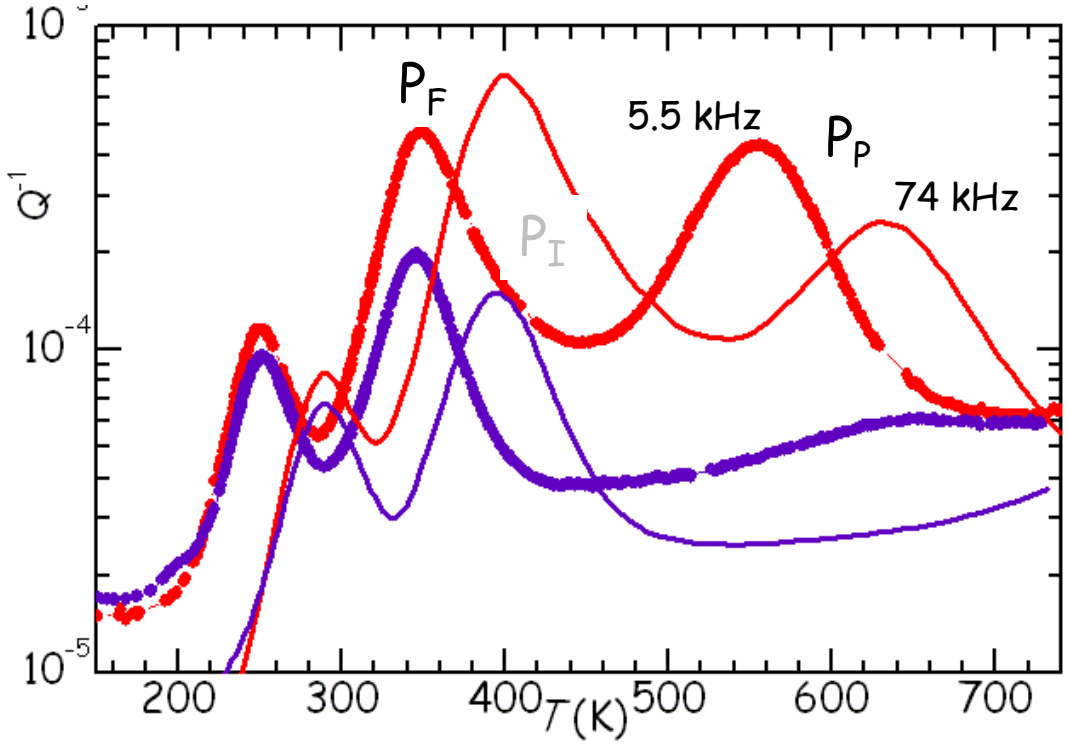
The creation of V_O introduces five peaks:

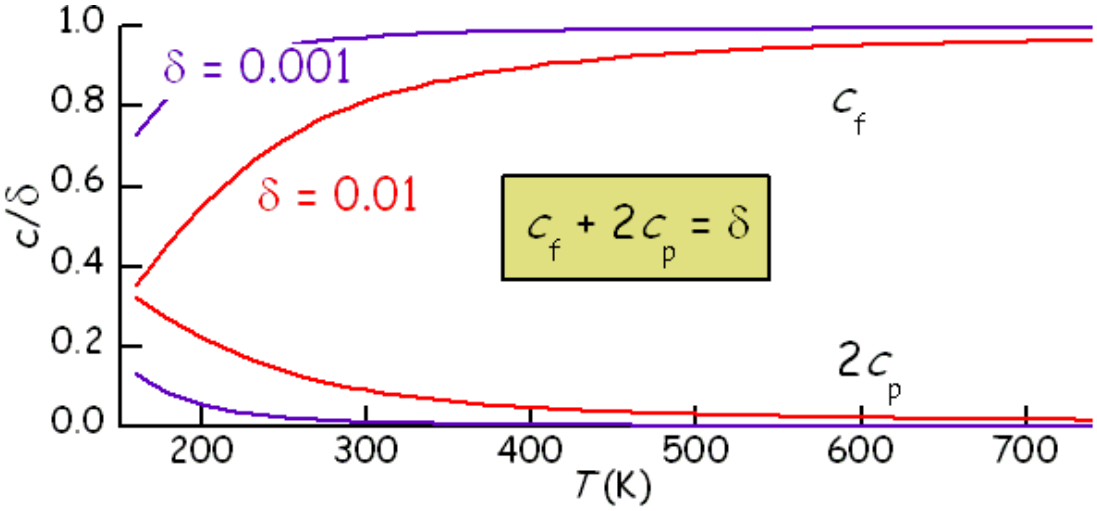
P_F-P_P grow considerably with increasing δ and therefore are due to V_O

P_5 saturates already at $\delta = 0.001$ and has a low activation energy: polarons?

F. Cordero, Phys. Rev. B 76, 172106 (2007)

Explanation of P1-P3 in terms of free and paired V_O





P_F: free V_O $\Delta(T) \propto c_f / T$

at low δ only $c_f \sim \delta$

P_P is absent

P_F decreases as $1/T$

at high δ $c_f = \delta - 2c_p$

pairs dissociation →

$c_p(T)$ is a decreasing function

$c_f(T)$ is an increasing function

P_P: paired V_O $\Delta(T) \propto c_p / T$

$c_p(T)$ is a decreasing function

the intensity decreases faster than $1/T$

P_I: intermediate step of pair reorientation + other jumps

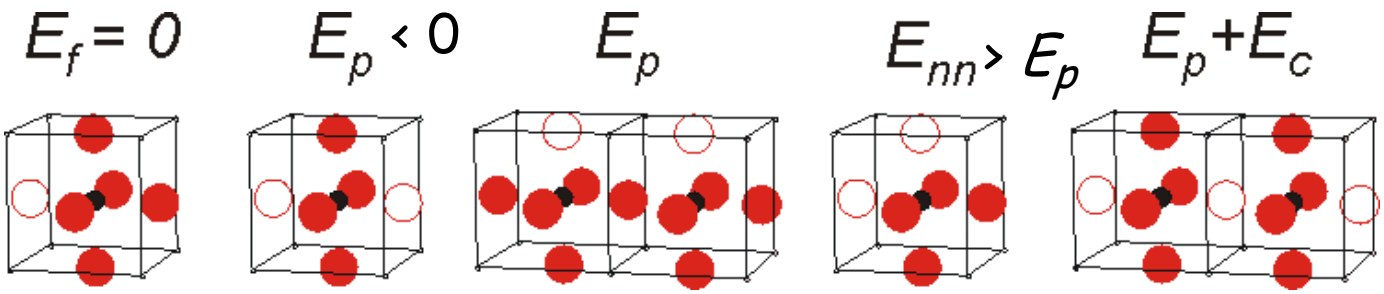
Statistical model for aggregated V_O

Subdivide the crystal into clusters of cells that are small enough to write their grandpartition function Z with all the possible configurations of V_O

(1) $$Z = \sum_\alpha w_\alpha = \sum_\alpha m_\alpha \exp\left(\frac{n_\alpha \mu - E_\alpha}{kT}\right)$$

(2) $$\mu: \quad \frac{kT}{Z}\frac{\partial Z}{\partial \mu} = \frac{\sum_\alpha n_\alpha w_\alpha}{\sum_\alpha w_\alpha} = \sum_\alpha \bar{n}_\alpha = \delta$$

n_α occupation number of α-th configuration
m_α multiplicity
E_α energy
w_α statistical weight
μ chemical potential from the implicit equation (2)



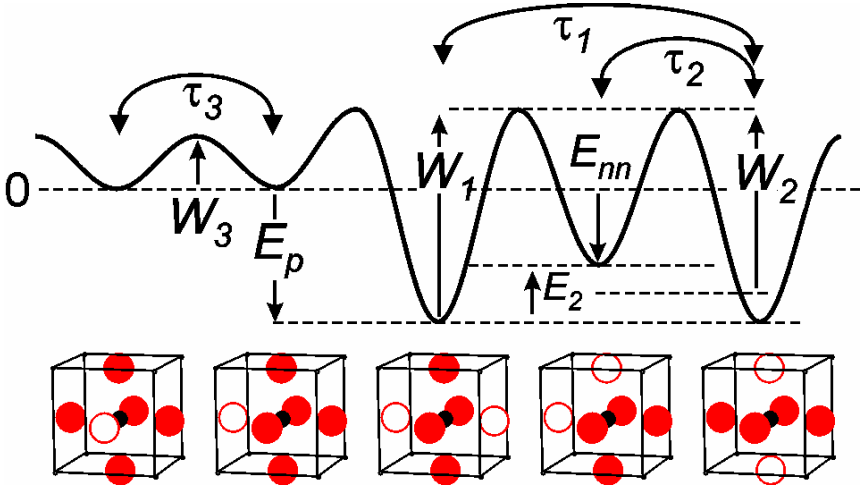
isolated (free)

stable pairs

nearest neighbours pair

chain

Anelastic relaxation



Three relaxations corresponding to P_F, P_P and P_I:

$$Q^{-1} = \frac{2}{9}\frac{cv_0}{s_{11}k_BT}(\Delta\lambda)^2\frac{\alpha(\omega\tau)^\alpha}{1+(\omega\tau)^{2\alpha}}$$

parameters:
W_1 = barrier for free hopping
W_3 = barrier for pair reorientation
W_2 = barrier for intermediate step
E_p = pair binding energy
E_c = binding of additional V into a chain
τ_0 = preexponential factors
α = Fuoss-Kirkwood broadening
$\Delta\lambda$ = change of elastic dipole for isolated V
$(\Delta\lambda)_1 \approx 2\Delta\lambda =$ " for pair reorientation

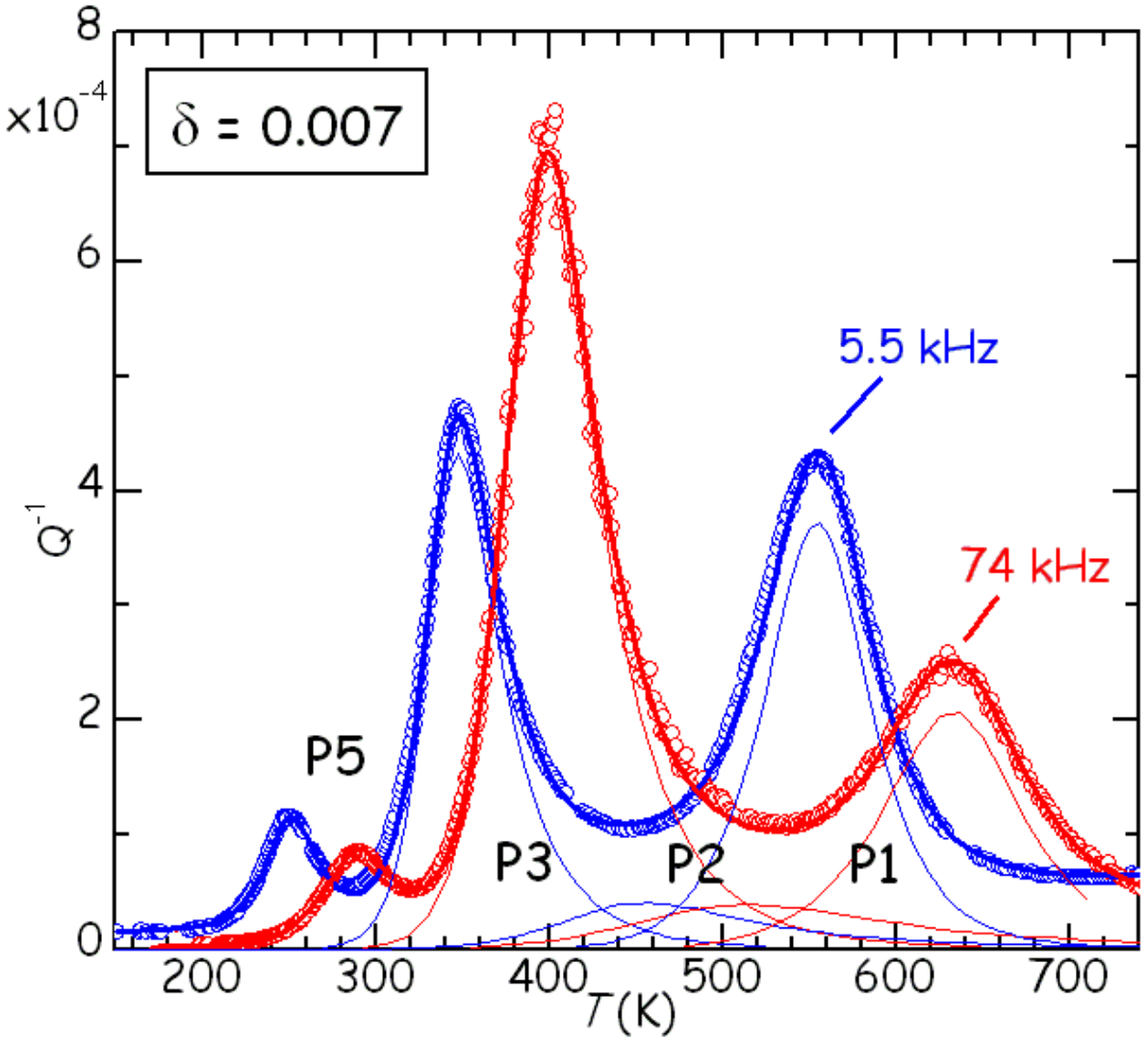
P2 between states differing by $E_2 = W_1 - W_2$:

$$\Delta(T) \propto \frac{c_p}{T\cosh^2(E_2/2kT)}$$

$$\tau^{-1} = \tau_0^{-1}\exp(-W_2/kT)\cosh(E_2/2kT)$$

routines for calculating μ, concentrations, and Q^{-1} peaks written in Origin C and integrated in the non linear fitting tool

Fit



same parameters for all $\delta > 0.001$!

other configurations contribute to P2: → $c > c_P$ and $(\Delta\lambda)_P \sim (\Delta\lambda)_F$

binding energies

$E_P = 0.184$ eV

$E_C = 0.26$ eV

free isolated V_O (P_F)

$c = c_F$

$W_F = 0.60 \pm 0.007$ eV

$\tau_{0F} = (5 \pm 1)\times10^{-14}$ s

$\alpha \geq 0.95$

$(\Delta\lambda)_F = 0.026$

pair reorientation (P_P)

$c = c_P$

$W_P = 0.97 \pm 0.04$ eV

$\tau_{0P} = (7 \pm 4)\times10^{-14}$ s

$\alpha \geq 0.95$

$(\Delta\lambda)_P = 1.87\times(\Delta\lambda)_F$

intermediate (P_I)

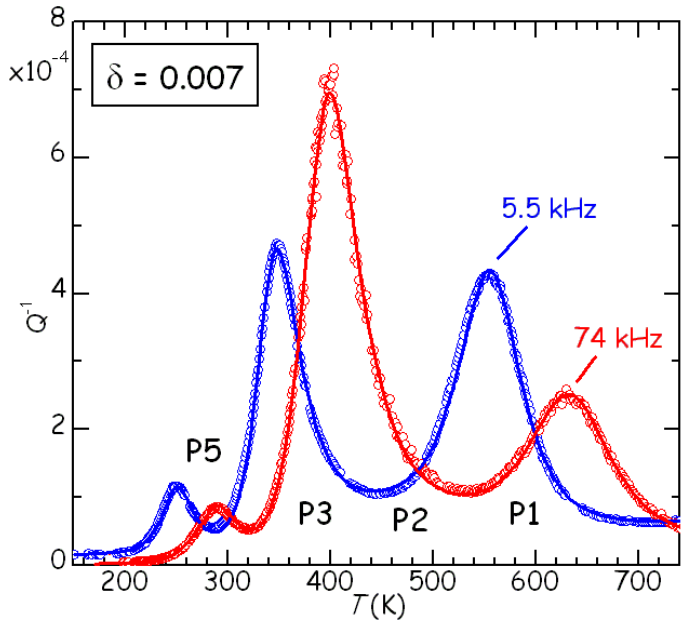
$c = c_P$

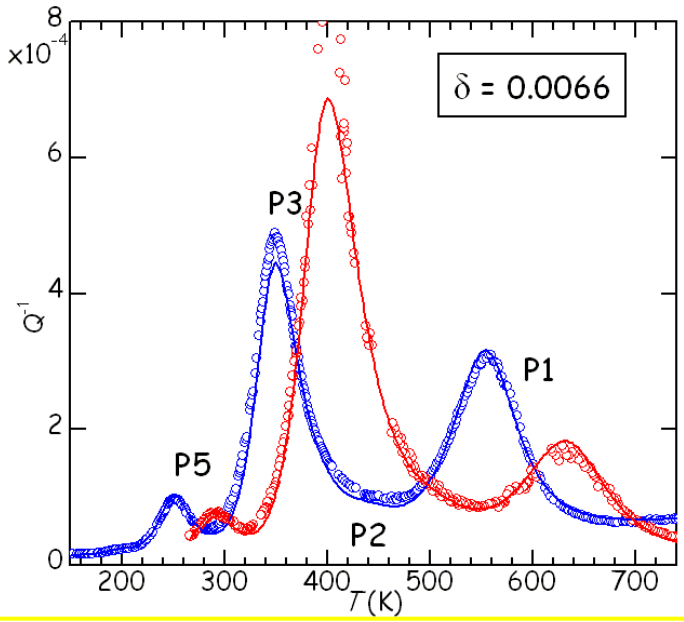
$W_P \sim 0.86$ eV

$\alpha \sim 0.35$

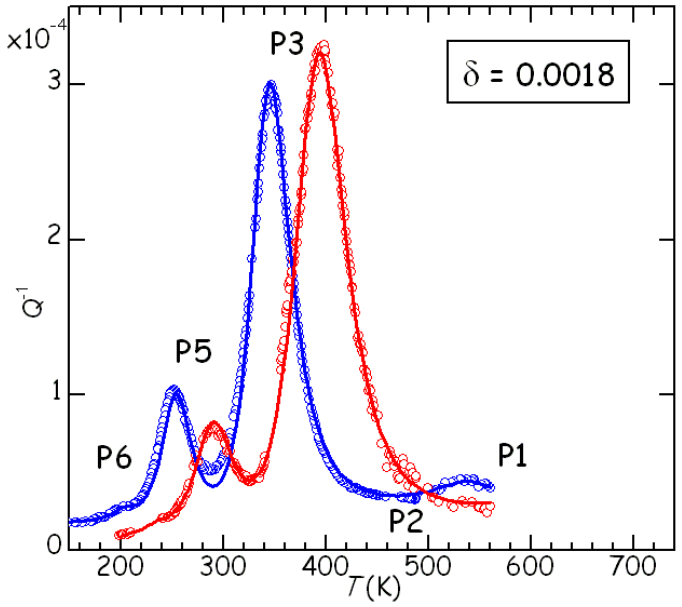
$(\Delta\lambda)_P = 5\times(\Delta\lambda)_F$

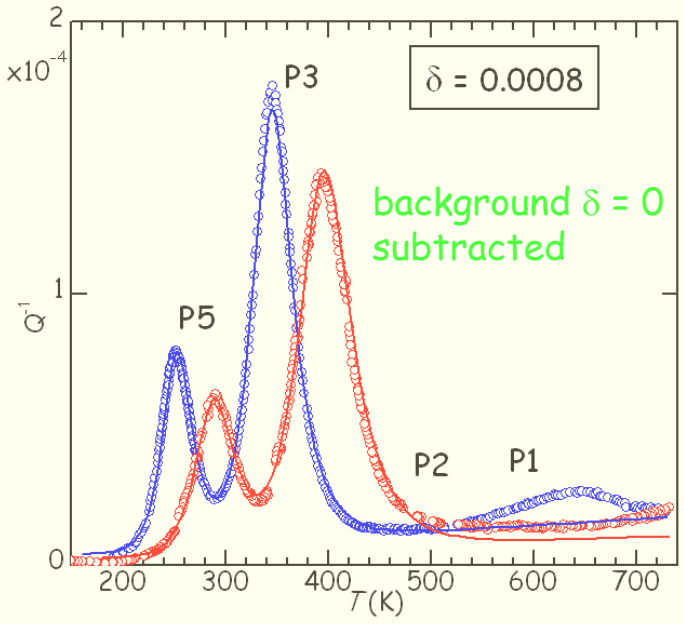
Fit





same parameters for all $\delta > 0.001$





$\delta = 0.00064$ instead of 0.0008 estimated from T_C

$E_p = 0.1$ eV instead of 0.18 eV

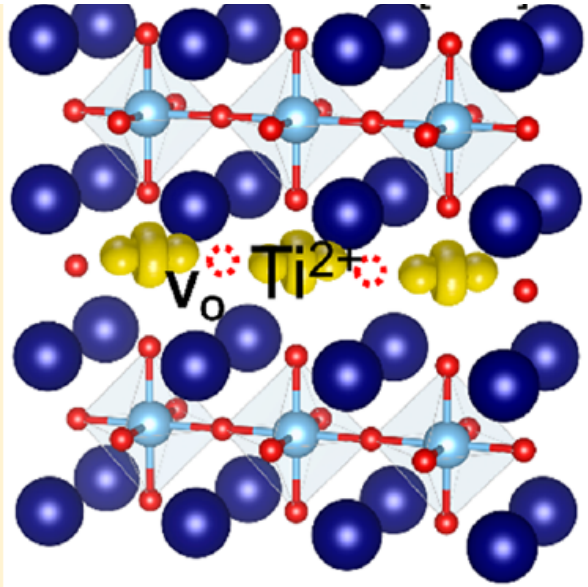
Confirmations from other recent experiments: V_O pairs

Highly O deficient $SrTiO_3$ films obtained by PLD at low p_{O2}

V_O-Ti^{2+}-V_O pairs

diffuse X-ray scattering: linear defects

Photoemission spectroscopy : Ti^{2+}



Eom *et al.* "Oxygen Vacancy Linear Clustering in a Perovskite Oxide"
J. Phys. Chem. Lett. 8, 3500 (2017)

Confirmations from other studies: hopping barrier of V_O

Method		$\Delta H_{mig,V}$ (eV)
Isotope diffusion		0.6
Isotope exchange		1.13
Chemical diffusion		0.98
Chemical diffusion		0.3
Isotope exchange		1.06
Chemical diffusion	$\delta < 5\times10^{-4}$	0.65
Chemical diffusion		2.1
Electrical conductivity		1.0
Nuclear-spin relaxation		0.62
Electrical conductivity		0.86
Anelastic relaxation	paired	0.98
Anelastic relaxation	isolated	0.60
Electrical conductivity		1.4
Thermally stimulated relaxation		0.91
C: Empirical pair potentials		0.65
C: Empirical pair potentials		0.76
C: Density functional theory		0.4 – 0.7
C: Empirical pair potentials		0.9
C: Density functional theory		0.6
C: Density functional theory		0.6
C: Empirical pair potentials		0.96 – 1.35

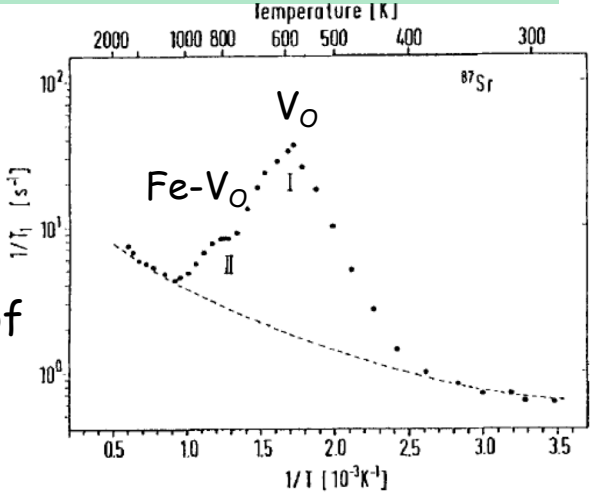
Metlenko, De Souza, Park and Weirich "Behavior of oxygen vacancies in single-crystal $SrTiO_3$: Equilibrium distribution and diffusion kinetics" Phys. Rev. B 85, 174109 (2012)

Schwarz and Anderson, J. Electrochem. Soc. 122, 707 (1975)

Hackmann and Kanert, Radiat. Eff. Defects Solids, 119–121, 651 (1991)

Cordero, Phys. Rev. B 76, 172106 (2007)

NSR rate $1/T_1$ of the nuclei is analogous to Q^{-1}



Confirmations from other studies: hopping barrier of V_O

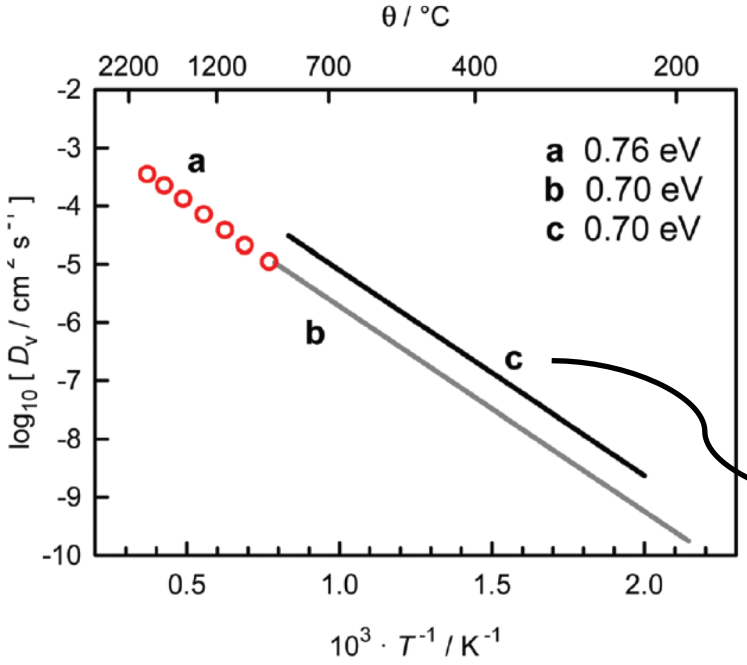
V. Metlenko, … , R. Waser, R. De Souza, Nanoscale 6, 12864 (2014)

	$\Delta H_{mig,V_O}$/eV	Ref.
EPP calculations	0.63	This study
DFT calculations	0.53	43
DFT calculations	0.51	44
DFT calculations	0.58	45
Isotope diffusion	0.62 ± 0.08	29
Nuclear spin relaxation	0.62	46
Anelastic relaxation	0.60 ± 0.007	47
Chemical diffusion	0.65 ± 0.06	48

43 Walsh *et al.*, Phys. Rev. B 83 220301 (2011)
44 T. Mizoguchi *et al.* Appl. Phys. Lett. 98, 091909 (2011)
45 M. Lontsi-Fomena *et al.* Comput. Mater. Sci. 44, 53 (2008)
46 Hackmann and Kanert, Radiat. Eff. Defects Solids, 119–121, 651 (1991) NMR
47 F. Cordero, Phys. Rev. B 76, 172106 (2007) anelastic
48 Schwarz and Anderson, J. Electrochem. Soc. 122, 707 (1975) $\delta < 5 \times 10^{-4}$

Most reliable studies on the hopping of V_O in $BaTiO_3$

J. Kaub, J. Kler, S. C. Parker and R. A. De Souza, Phys. Chem. Chem. Phys. 22, 5413 (2020)



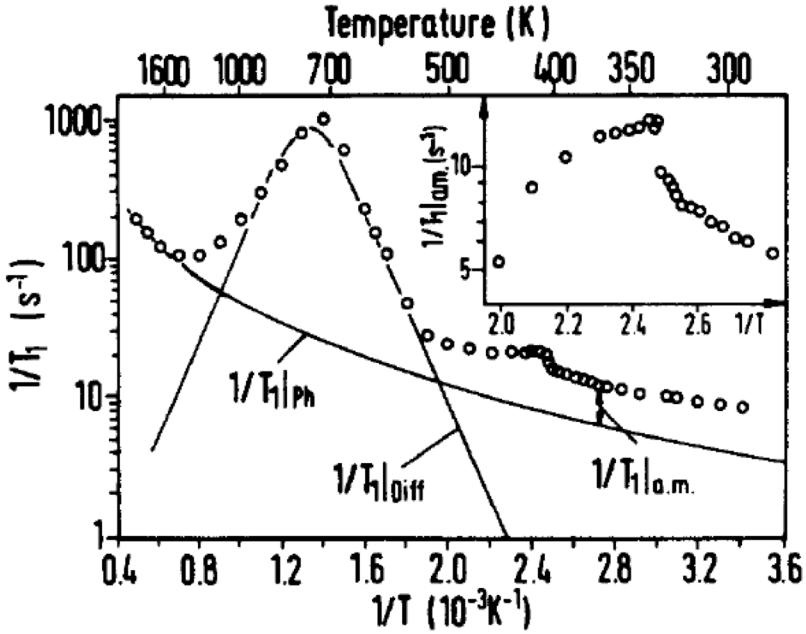
activation enthalpy of migration of V_O in $BaTiO_3$ from

a) isotope exchange: 0.70eV

b) molecular dynamics simulations: 0.76 eV

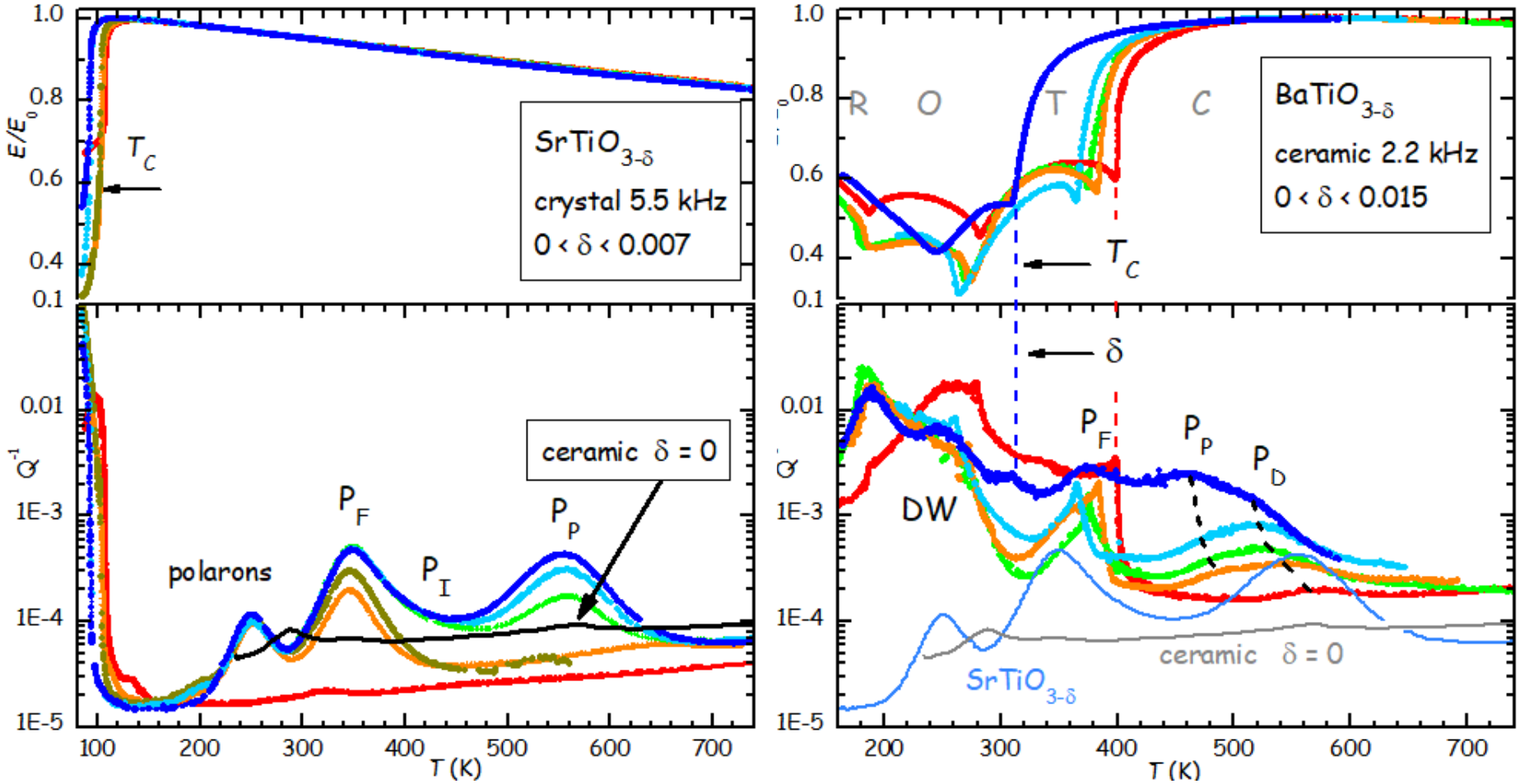
c) NMR: 0.70eV

Kanert *et al.* Solid State Commun. 91, 465 (1994)



Maier and Randall
J. Am. Ceram. Soc. 99, 3360 (2016)
impedance spectroscopy: 0.70eV

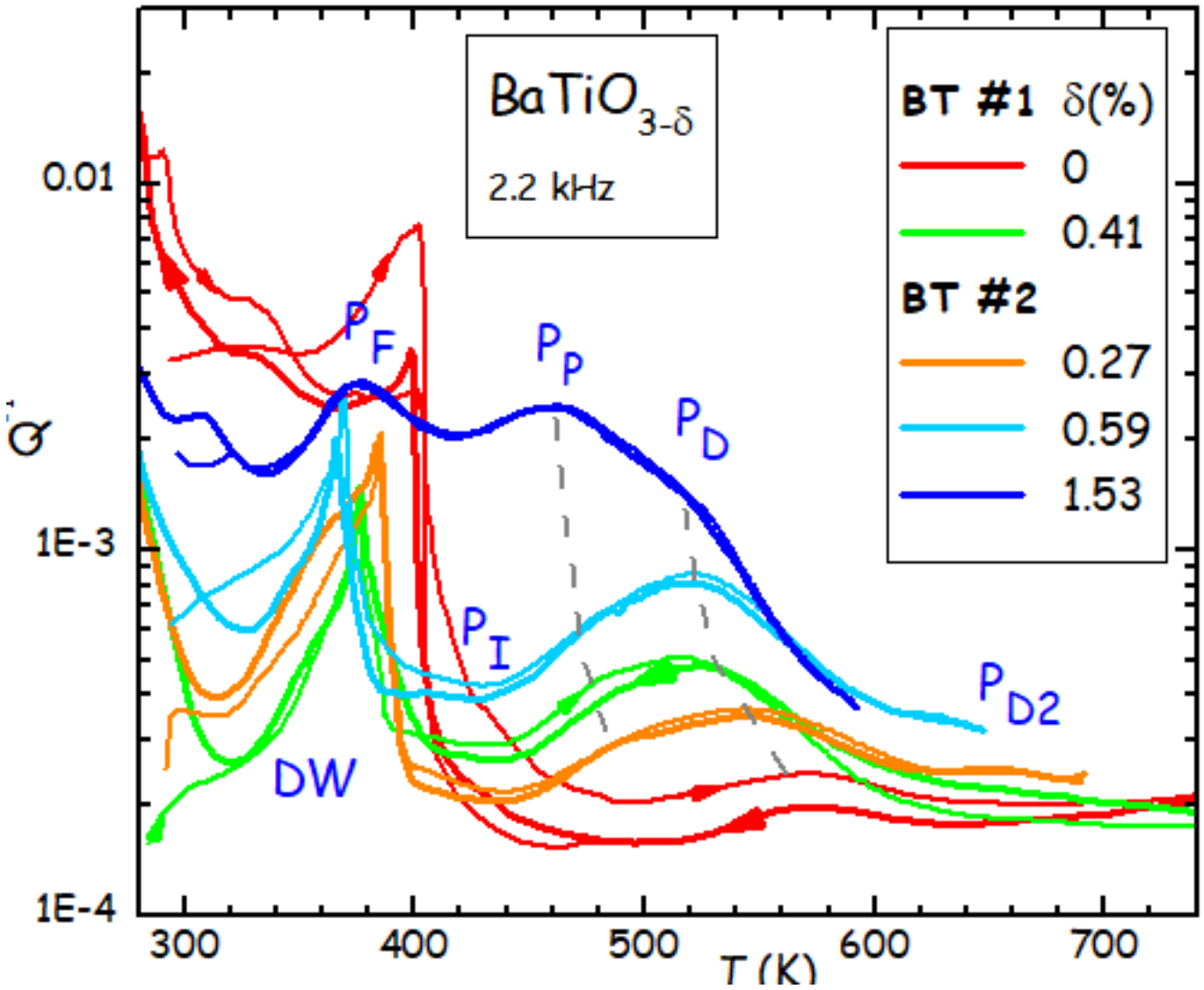
Anelastic spectra of $BaTiO_{3-\delta}$ vs $SrTiO_{3-\delta}$



- precursor softening due to phase transitions (deviation from stiffening linear with T) already below 800 K
- higher background dissipation ceramic vs single crystal?)
- T_C decreases with O deficiency until at $\delta = 0.017$ also P_F from isolated V_O is visible
- increasing δ all the thermally activated peaks increase the intensity and shift to lower T

F. Cordero, F. Trequattrini, D.A.B. Quiroga, P.S. Silva Jr., J. Alloys and Compounds 874 159753 (2021)

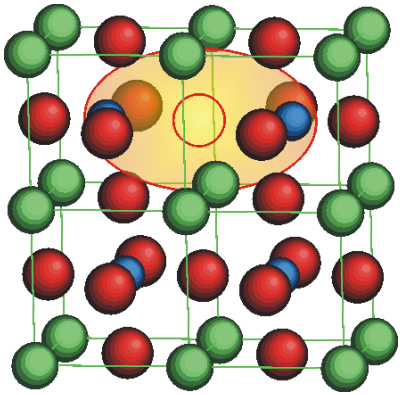
Stability of the anelastic spectrum of $BaTiO_{3-\delta}$



thin splines = heat
thick splines = cool

Fitting functions

hopping of very diluted isolated V_O in ceramic:
orientational average of Debye relaxation



used to estimate $\Delta\lambda$

$$Q^{-1} = \underbrace{\frac{2}{15}\frac{cv_0E}{k_BT}(\Delta\lambda)^2}_{\Delta/T}\frac{\omega\tau}{1+(\omega\tau)^2}$$

each peak fitted with

$$Q^{-1} = \frac{\Delta}{T}\frac{\alpha(\omega\tau)^{\alpha}}{1+(\omega\tau)^{2\alpha}}$$

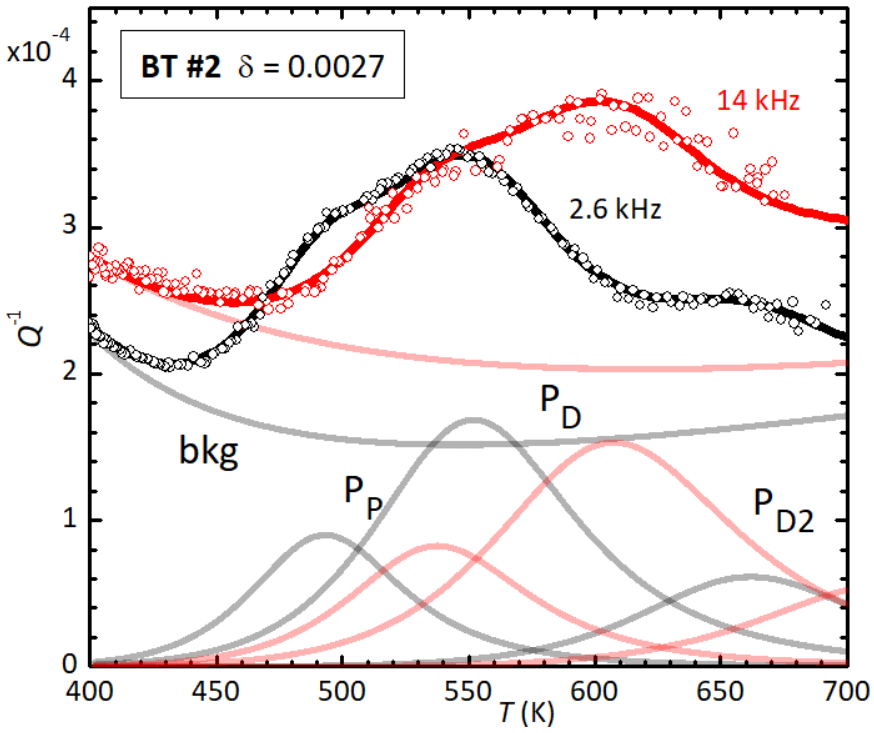
$\alpha \leq 1$ Fuoss-Kirkwood broadening

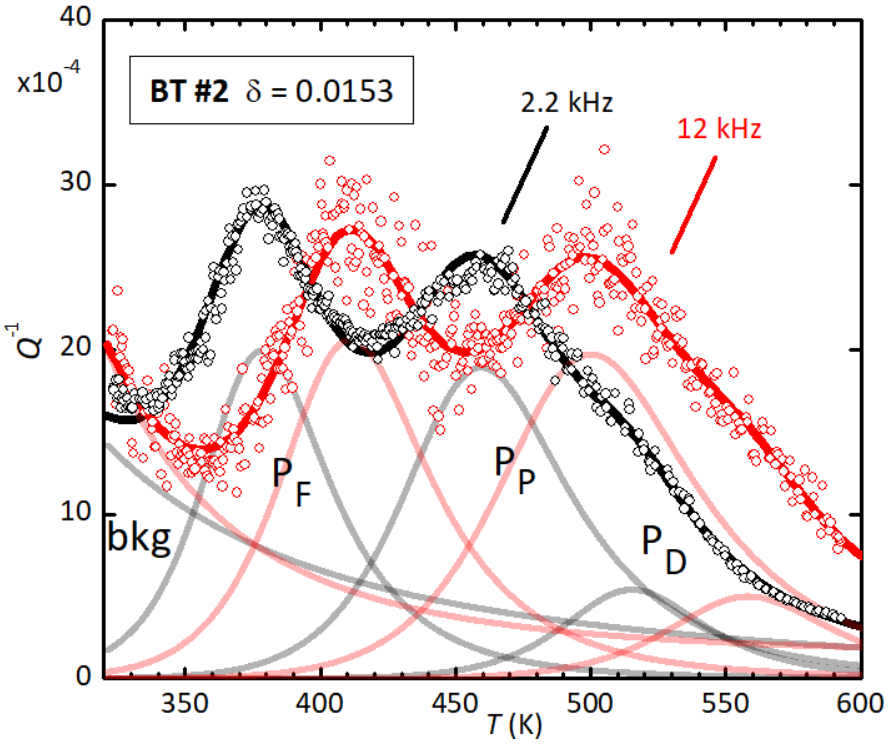
$$\Delta(T) \rightarrow \frac{\Delta}{T\cosh^2(A/2kT)}$$

$$\tau^{-1} = \tau_0^{-1}\exp(-W/kT)\cosh(A/2kT)$$

relaxation between states with energies differing of A

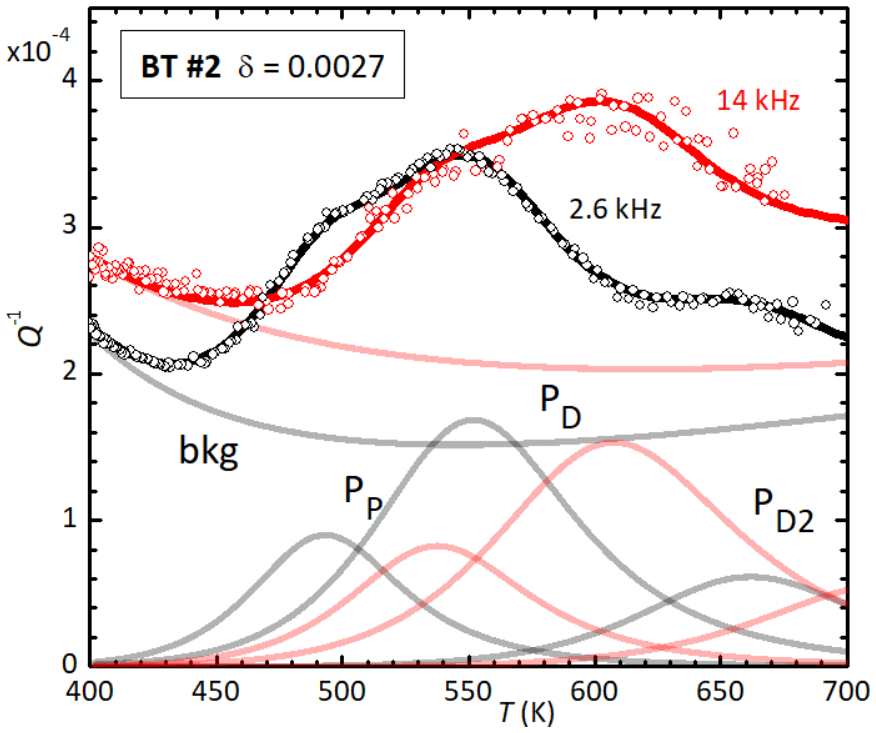
Fits of the anelastic spectra of $BaTiO_{3-\delta}$

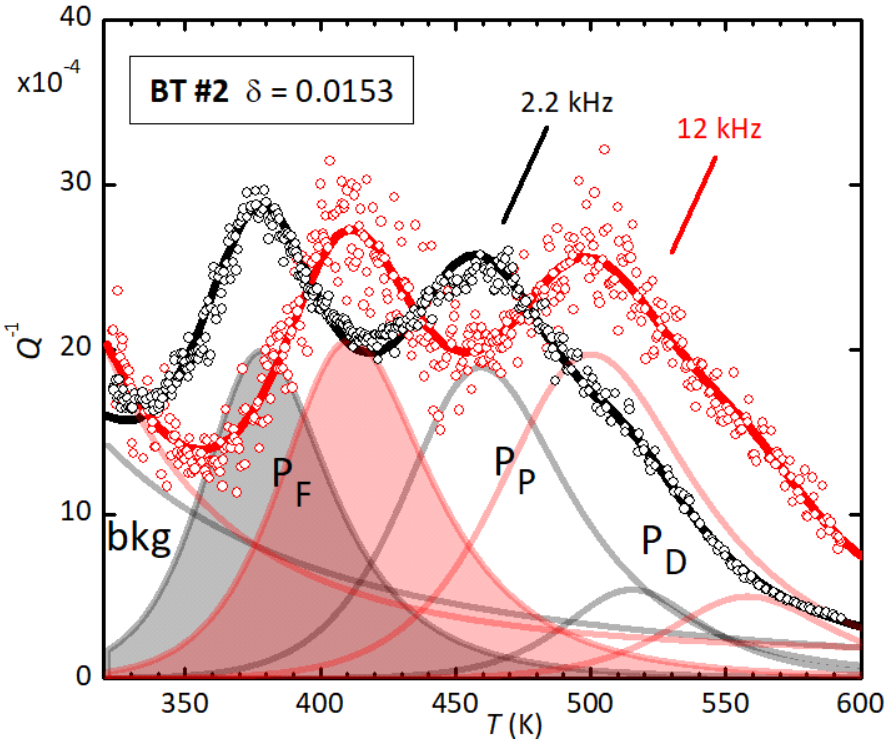




P_F : hopping of free V_O
P_P : reorientation of V_O pair
P_D : ($V_{Ba/Ti}$/impurity)-V_O pair
P_{D2} : other ($V_{Ba/Ti}$/impurity)-V_O pair

P_F: hopping of free V_O





NMR: Kanert *et al.*, Solid State Commun. 91, 465 (1994);
Impedance spectr.: Maier and Randall, J. Am. Ceram. Soc. 99, 3360 (2016);
Isotope exchange: J. Kaub *et al.*, Phys. Chem. Chem. Phys. 22, 5413 (2020)

V_O migration in $BaTiO_3$: W = 0.70 eV

$\delta = 0.0153$

W = 0.72 eV ($SrTiO_3$: 0.60 eV)

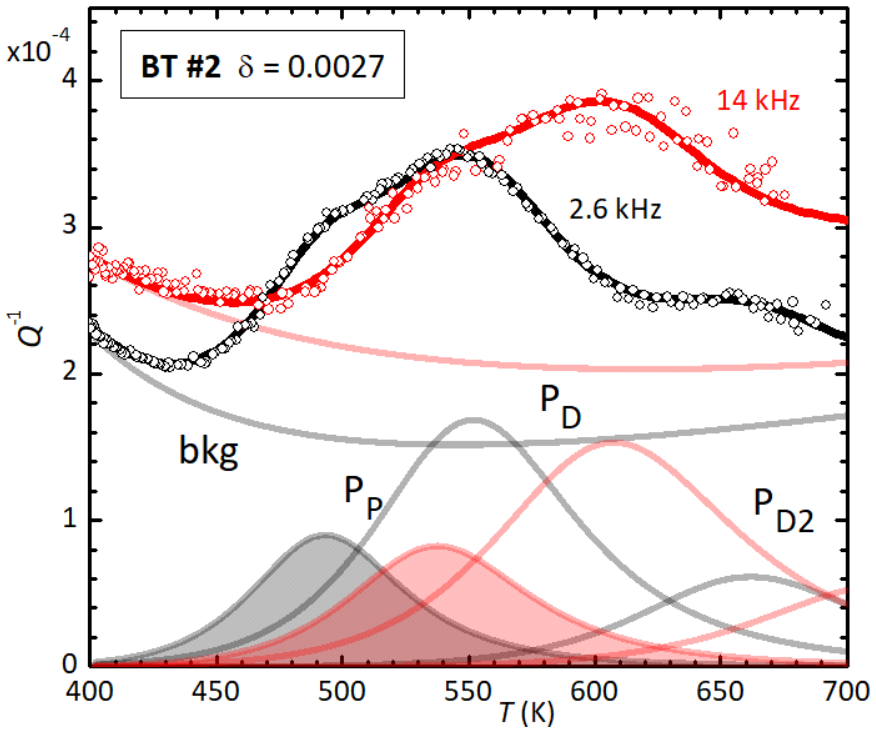
$\tau_0 = 2.6\times10^{-14}$ s point defect

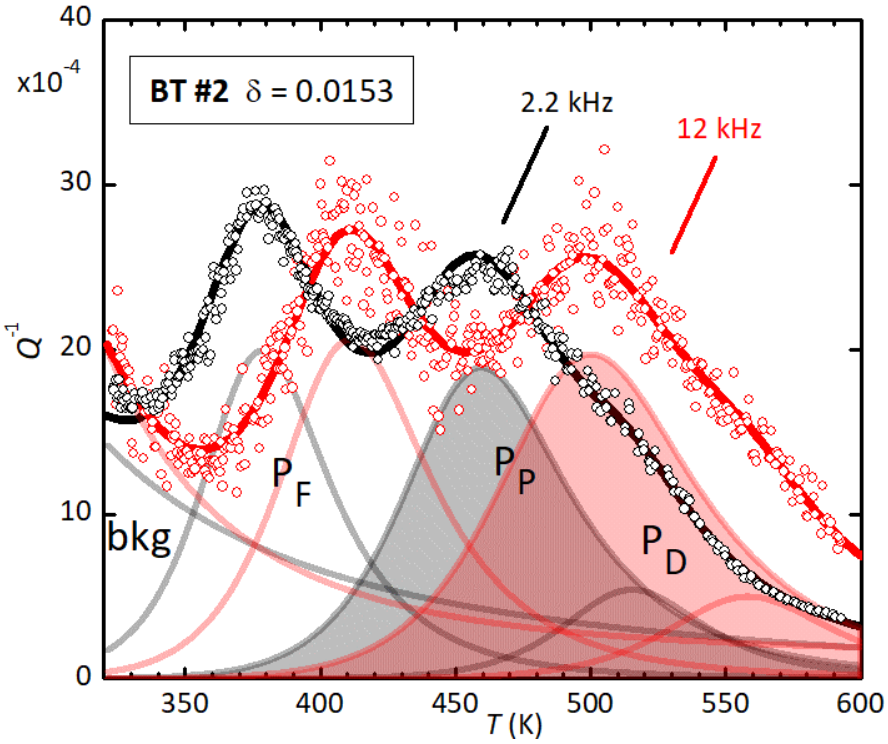
$\alpha = 0.84$ } single Debye

$A/k_B = 7.4$ K ~ 0 }

$\Delta = 3.51$ K $\rightarrow \Delta\lambda = 0.077$ ($SrTiO_3$: 0.026)

P_P: reorientation of V_O pair





W = 0.87 eV (SrTiO$_3$: 0.97 eV)

$\tau_0 = 9.0\times10^{-14}$ s point defect

α = 0.91

A/k_B = 0 K

Δ = 0.0888 K

W = 0.85 eV

$\tau_0 = 4.7\times10^{-14}$ s

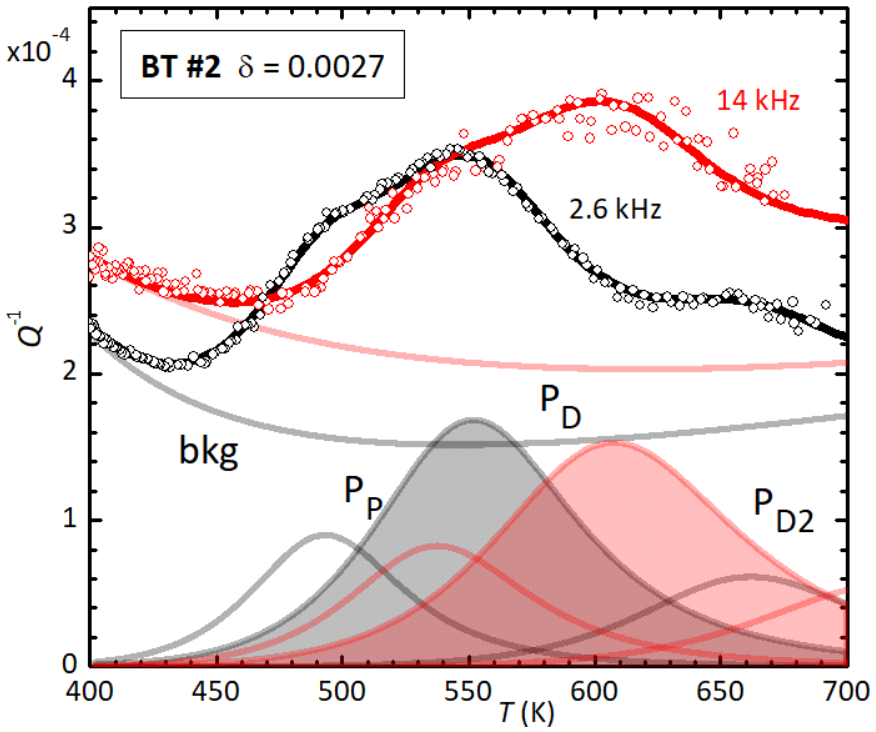
α = 0.80

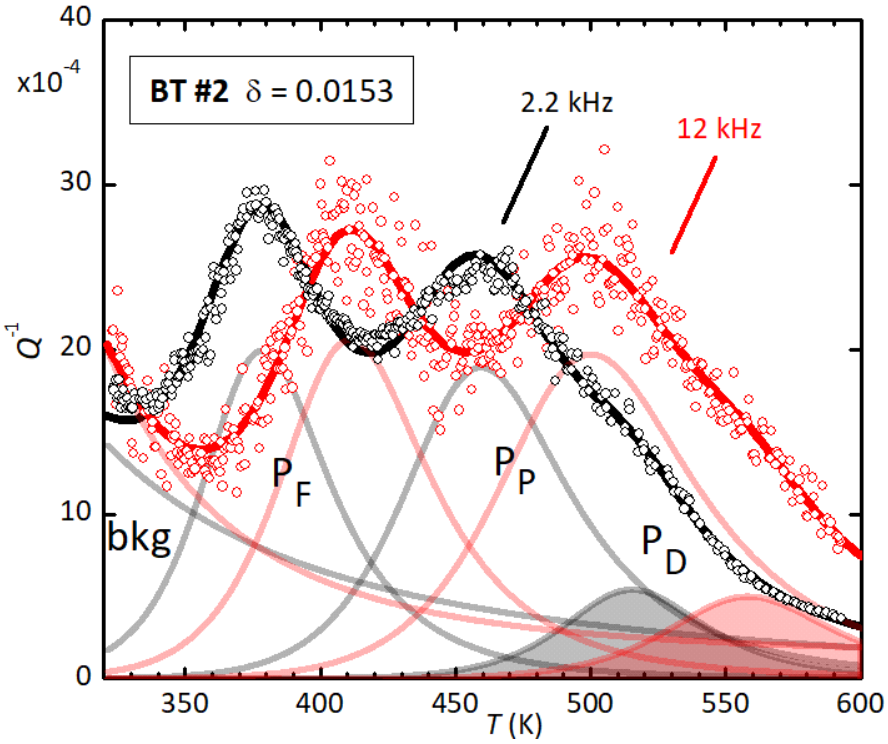
A/k_B = 940 K

Δ = 4.29 K

$$\frac{\Delta(\delta=0.0153)}{\Delta(\delta=0.0027)} = 48 = 1.5 \times \left(\frac{0.0153}{0.0027}\right)^2$$

P_D: defect-V_O pair





W = 0.87 eV (SrTiO$_3$: 0.97 eV)

$\tau_0 = 7.1\times10^{-13}$ s point defect

$\alpha = 1$

$A/k_B = 0$

$\Delta = 0.186$ K

W = 0.97 eV

$\tau_0 = 2.2\times10^{-14}$ s

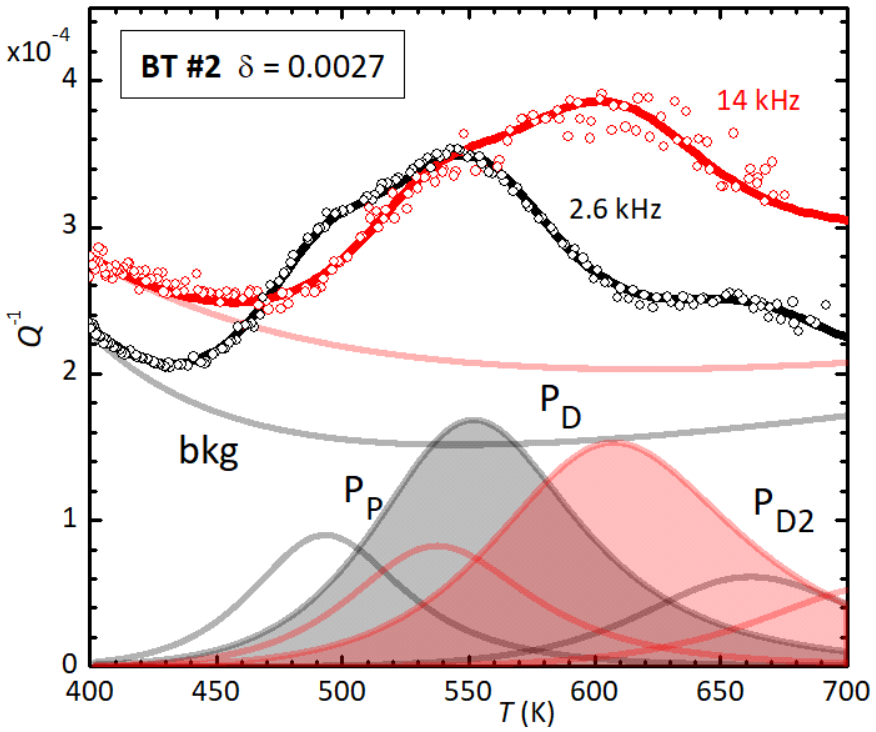
$\alpha = 1$

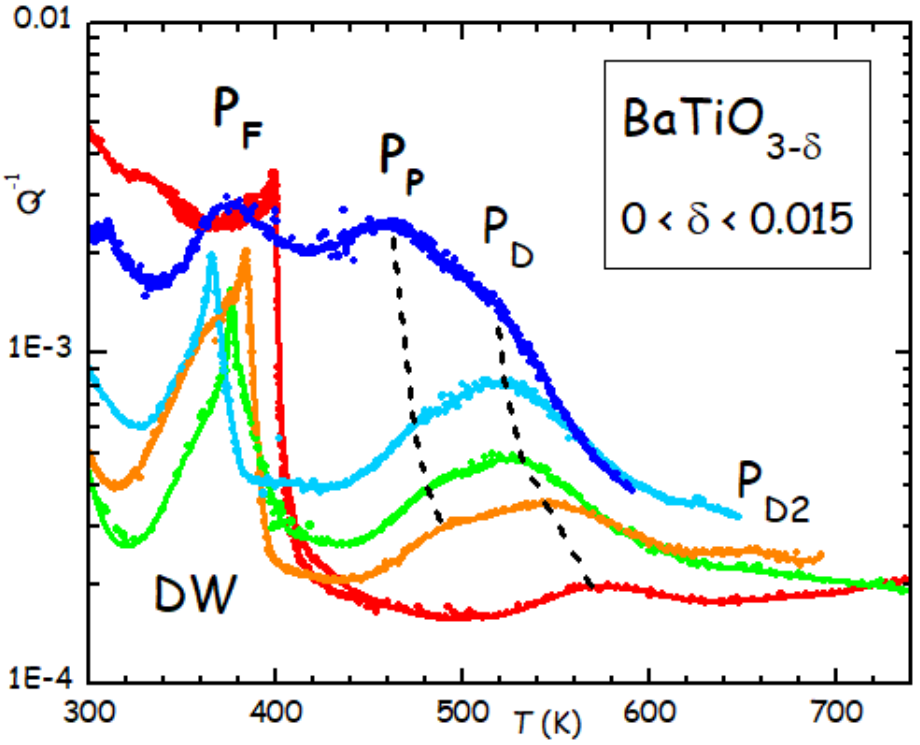
$A/k_B = 0$

$\Delta = 0.557$ K

defect: V_{Ba} or V_{Ti} or acceptor impurity

P_D: defect-V_O pair





W = 0.87 eV

$\tau_0 = 7.1\times10^{-13}$ s

$\alpha = 1$

$A/k_B = 0$

$\Delta = 0.186$ K

($SrTiO_3$: 0.97 eV)

point defect

W = 0.97 eV

$\tau_0 = 2.2\times10^{-14}$ s

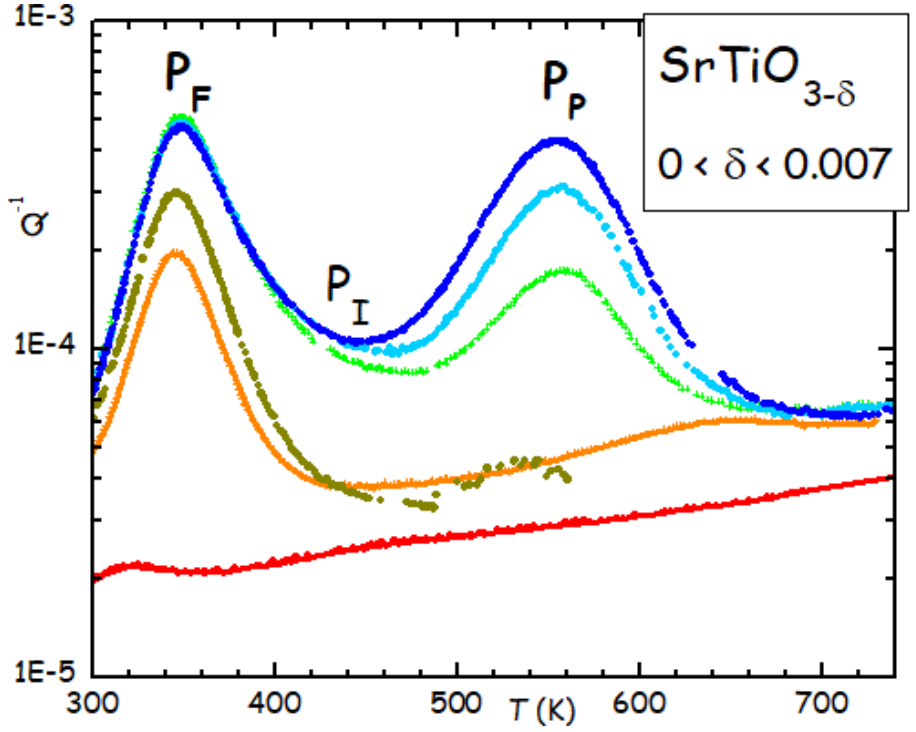
$\alpha = 1$

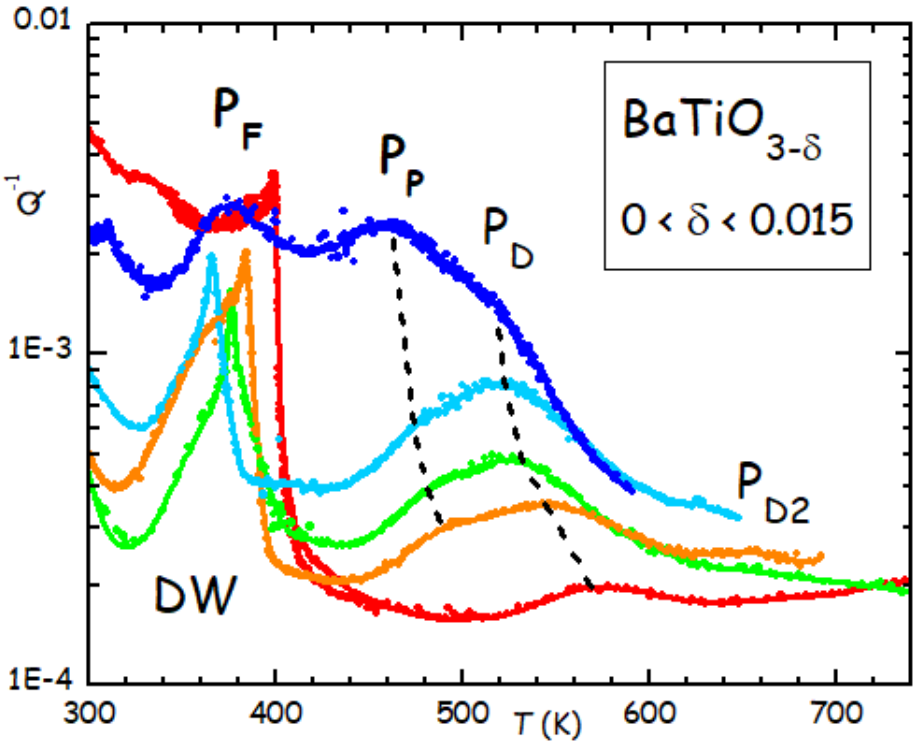
$A/k_B = 0$

$\Delta = 0.557$ K

defect: V_{Ba} or V_{Ti} or acceptor impurity

Why the differences between $BaTiO_{3-\delta}$ and $SrTiO_{3-\delta}$?





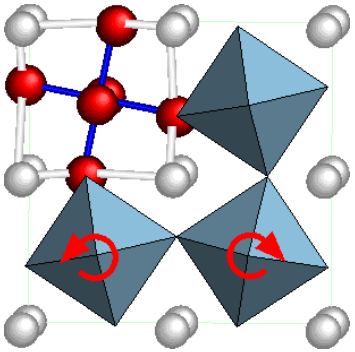
elastic dipole of isolated V_O from the intensity of P_F:

$\Delta\lambda = 0.026$ $\Delta\lambda = 0.077$

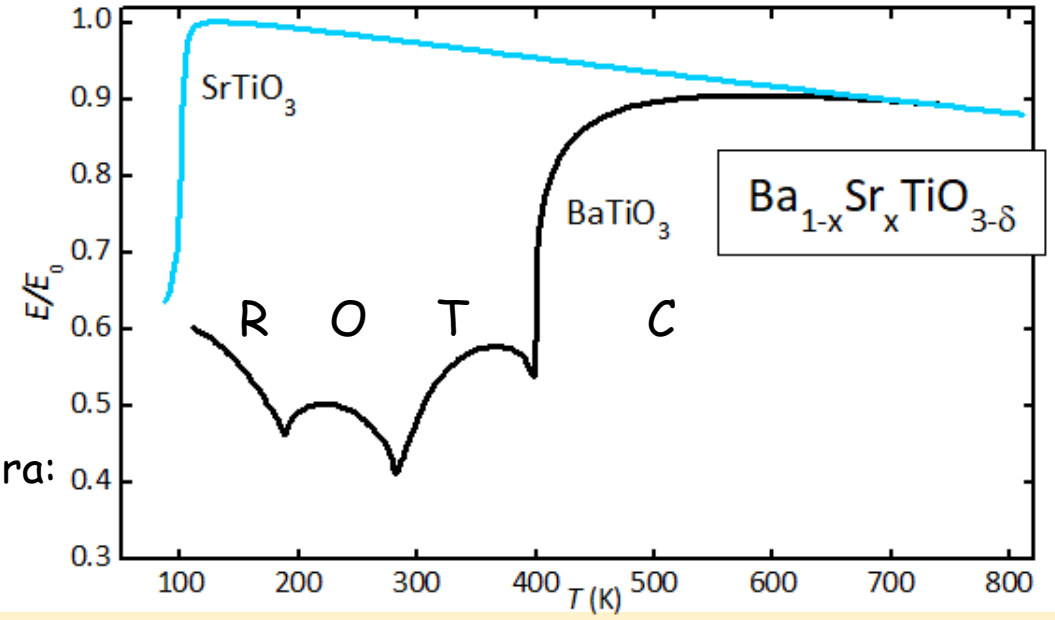
in $BaTiO_{3-\delta}$

- the peaks shift to lower *T* with increasing δ
- $\Delta\lambda$ is three times larger

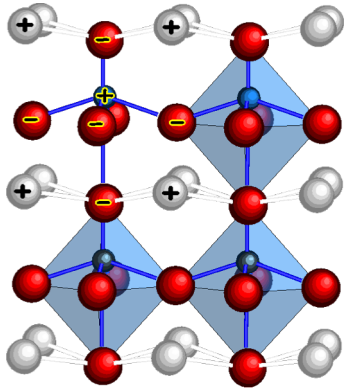
Phase transitions and Young's modulus of $Ba_{1-x}Sr_xTiO_{3-\delta}$



rotation of octahedra:
antiferrodistortive
non-polar



P



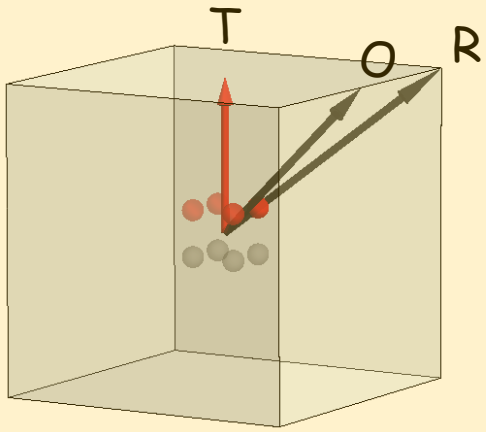
ferroelectric mode
with polarisation ***P***

Eight-site model

Mason and Matthias, Phys. Rev. 74 1622 (1948); Devonshire (1949)

…

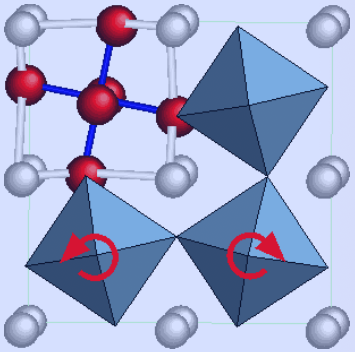
Bersuker, Phys. Lett. 20, 589 (1966); Chem. Rev. 121, 1463 (2021):
pseudo- Jahn-Teller effect where the electronic energy is lowered by the increase of covalency between Ti and the closest O atoms.
Experimental confirmations: diffuse XRD, EXAFS, NMR, EPR, Brillouin scattering



Correlated anharmonic vibrations of Ti

Hüller, Solid State Commun. 7 589 (1969) …

Softening at the phase transitions



rotation of octahedra:
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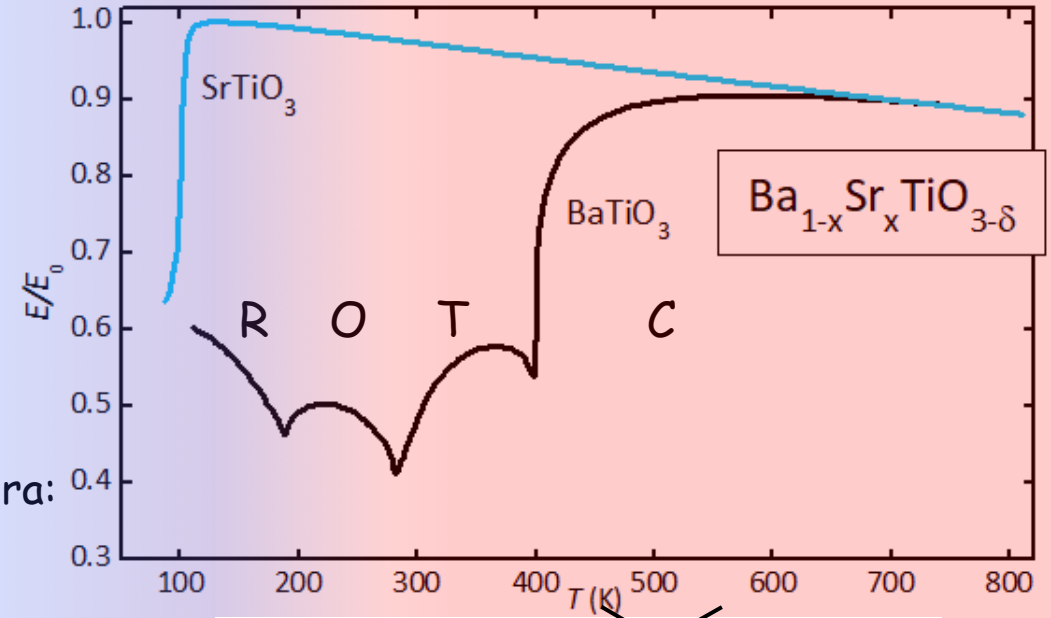
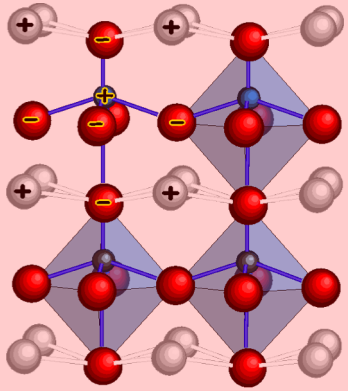




P

ferroelectric mode
with polarisation ***P***

$$*P^2 + *P^4 \ldots *\sigma^2 \ldots \cancel{*\sigma P} + *\sigma P^2 + \ldots$$

OP = ϕ ~ rotation angle

$$G = F(\phi) - \tfrac{1}{2} s_0 \sigma^2 - R\sigma\phi^2$$

OP = P ~ Ti displacement

$$G = F(P) - \tfrac{1}{2} s_0 \sigma^2 - Q\sigma P^2$$

same coupling of stress to OP → same elastic anomaly

compliance from
free energy:

$$F = \frac{a}{2}(T - T_C)P^2 + \frac{b}{4}P^4$$

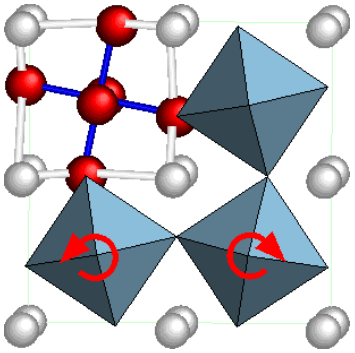
simplest expansion in powers of OP

$$E^{-1} = \frac{d\varepsilon}{d\sigma} = -\frac{\partial^2 G}{\partial \sigma^2} + \frac{d\varepsilon}{dP}\frac{dP}{d\sigma} = s_0 + 4\chi Q^2 P^2 = s_0 + 2Q^2/b$$

steplike softening at the transition

fluctuations in the cubic phase $4\chi Q^2\langle P^2\rangle$ precursor softening

Phase transitions and Young's modulus of $Ba_{1-x}Sr_xTiO_{3-\delta}$



rotation of octahedr
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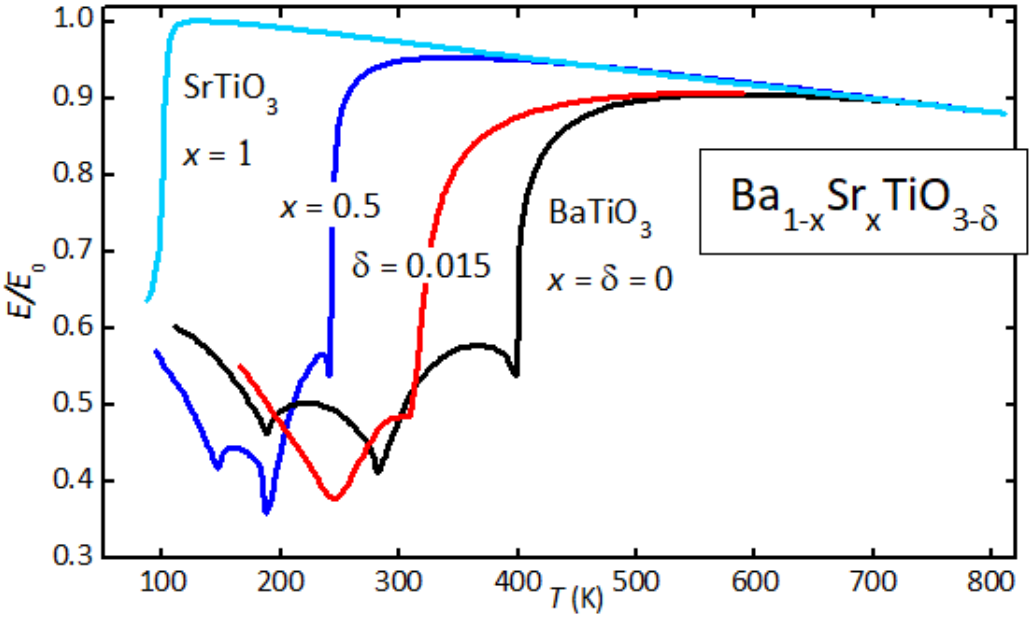
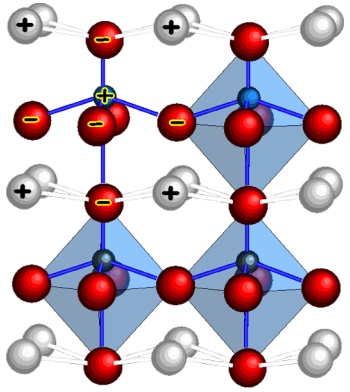
non-polar





ferroelectric mode
with polarisation ***P***

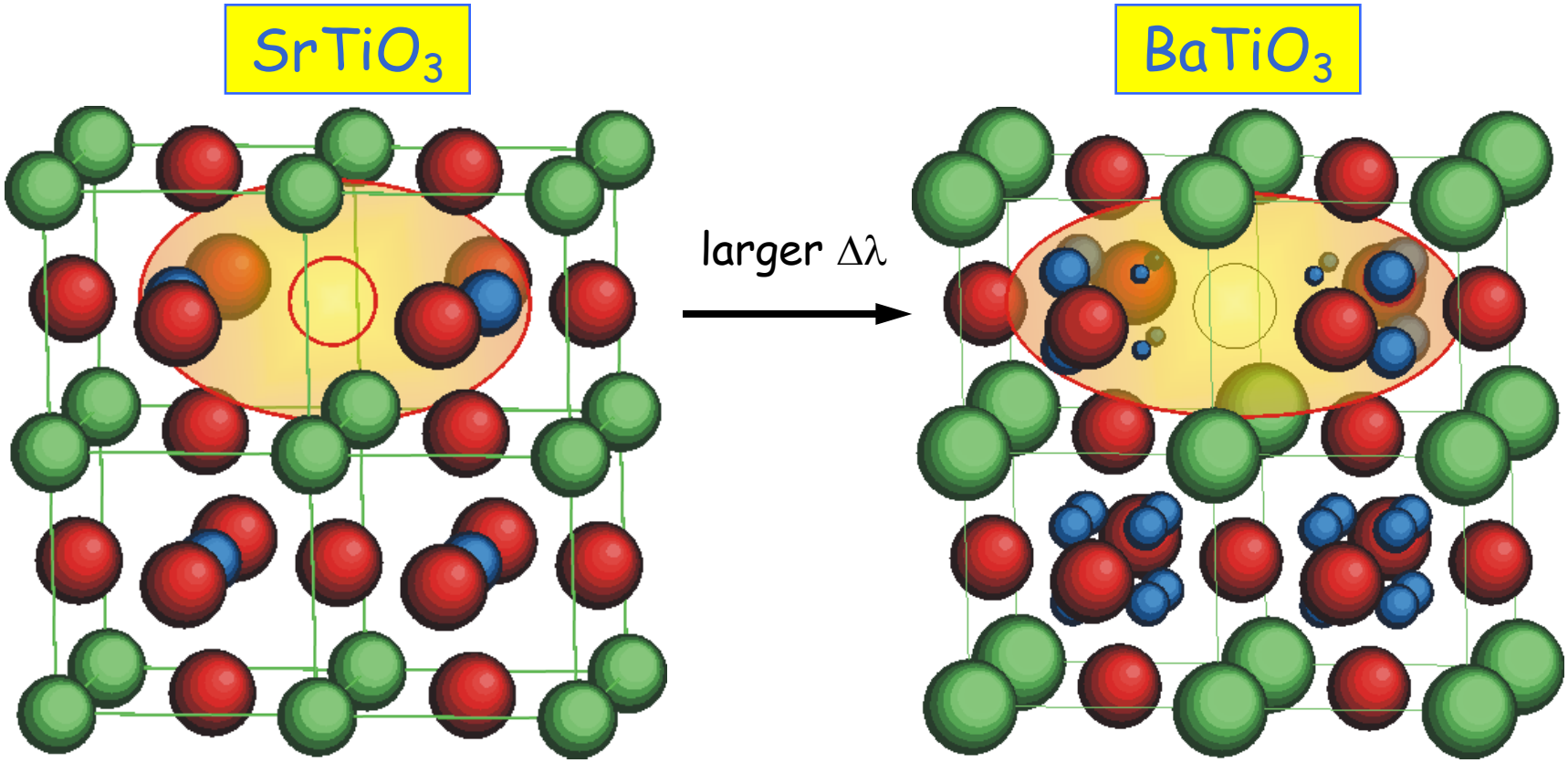
- Sr is only smaller than Ba but with the same orbitals
- V_O^{2+} is charged and dopes electrons: 1.5% V_O has an effect similar to 25% Sr

volume change of V_O uncertain/small; larger contribution from Ti^{4+}/Ti^{3+} polaronic conductivity, low *T* anelastic relaxations in $SrTiO_{3-\delta}$

Tyunina, Materials 13, 5596 (2020)

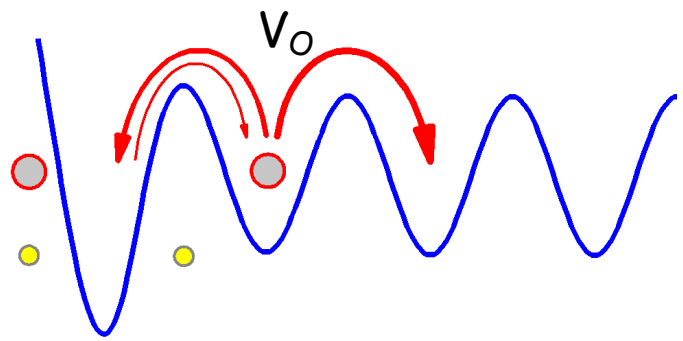
Magnitude of the elastic dipole of V_O

Major contribution to the anisotropy $\Delta\lambda$: the positively charged V_O pushes outwards the nn Ti^{4+} atoms. Easier in $BaTiO_3$

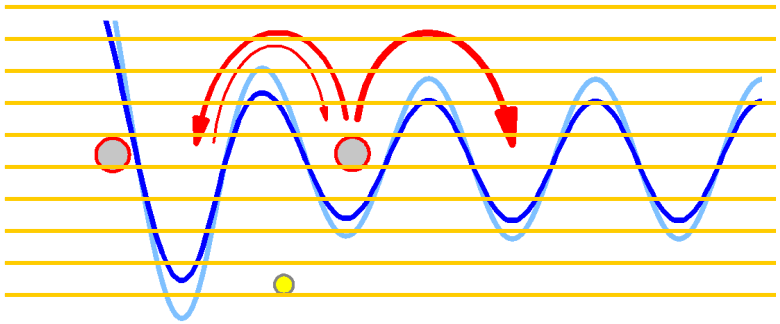


In $BaTiO_3$ the nn Ti atoms will populate the outward off-centre sites, increasing their outward displacement

Decrease of activation energies with doping

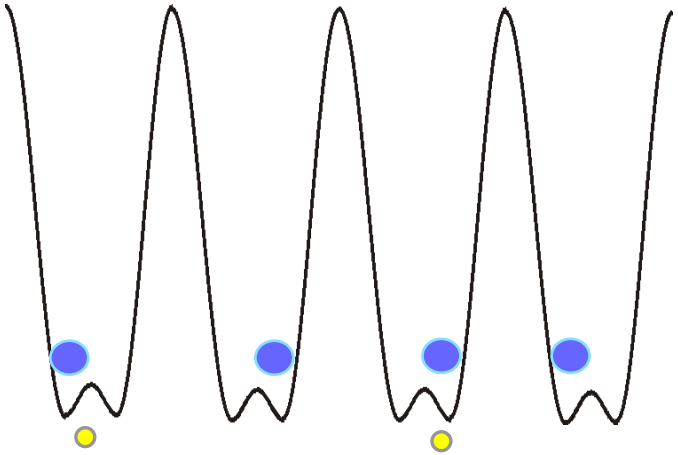


small polaron

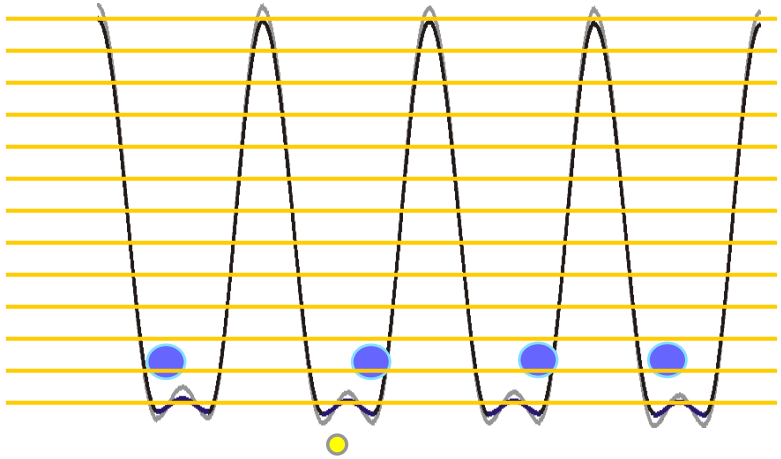


small polaron + band

the potential is washed out by screening → smaller barriers (also in $SrTiO_3$)



8 site potential for Ti



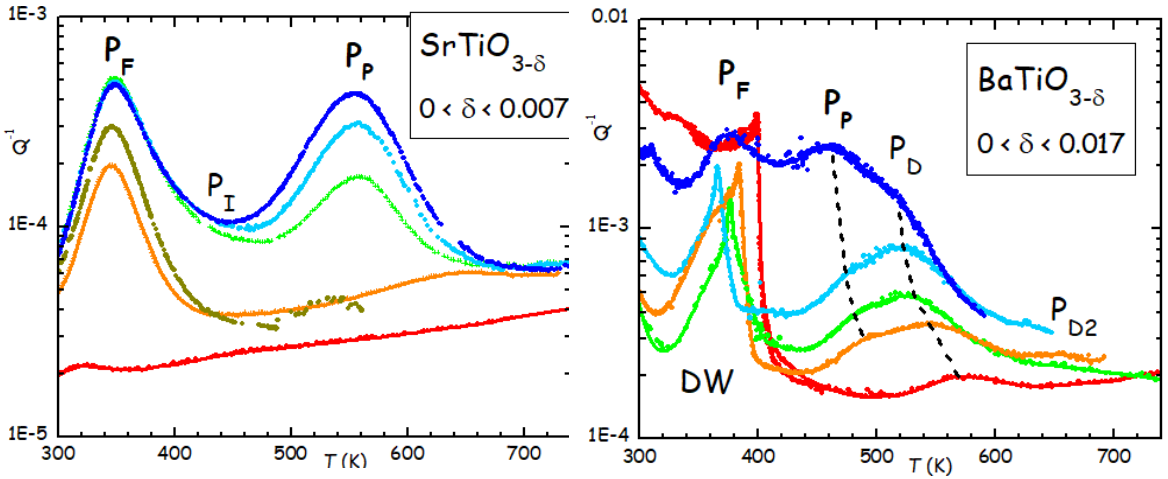
larger effect on the small barriers for Ti off-centre hopping, responsible for the lowering of T_C

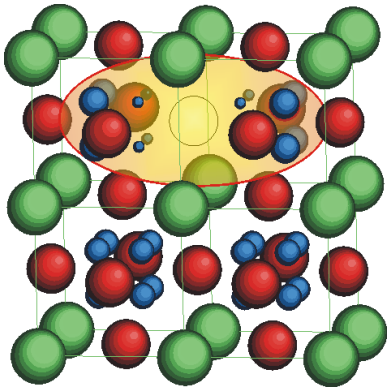
- Ti off-centering in undoped $BaTiO_3$ → larger relaxation around V_O → larger barrier and $\Delta\lambda$
- doping reduces off-centering and all these effects

Conclusions

The anelastic spectra of $BaTiO_{3-\delta}$ contain the same peaks due to isolated and paired V_O as $SrTiO_{3-\delta}$ but

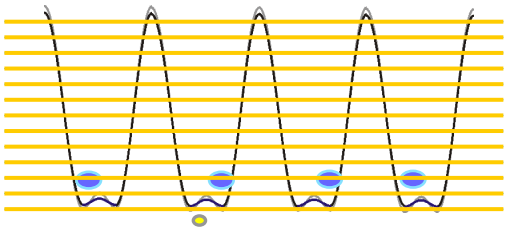
- the spectra shift much to lower T with increasing δ
- $\Delta\lambda$ of the isolated V_O is three times larger than in $SrTiO_{3-\delta}$
- the activation energy for single V_O hopping is
- the hopping barrier is 0.70 eV compared to 0.60 eV in $SrTiO_{3-\delta}$



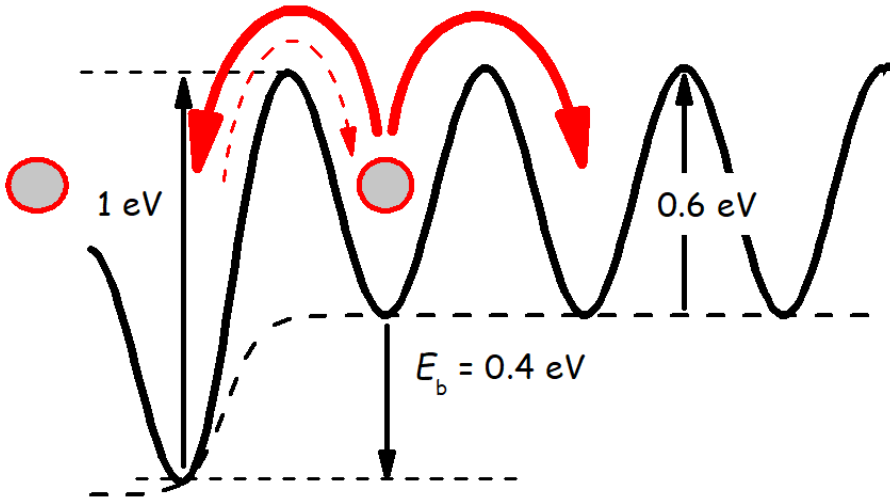


explanation in terms of 8 site potential of off-centre Ti, which

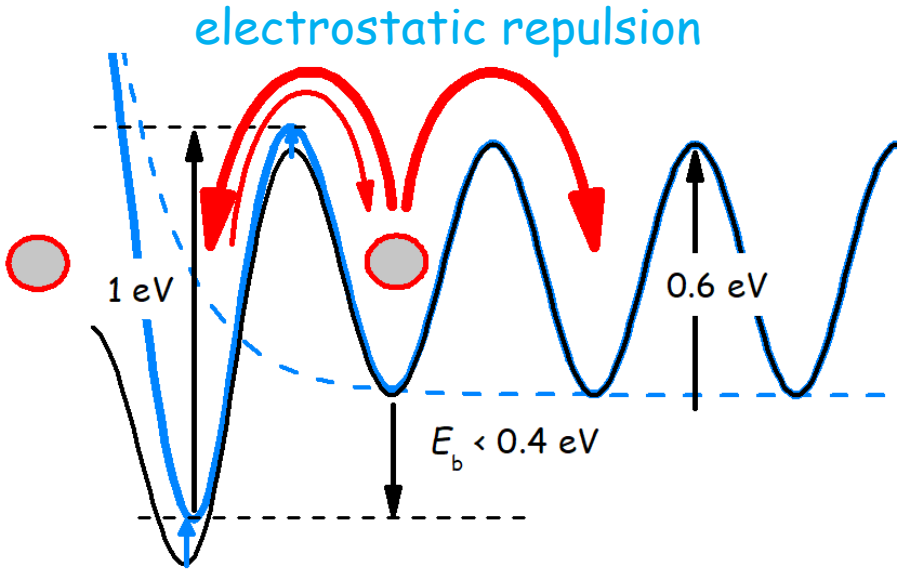
- enhances the outwards shifts of Ti from the V_O
- is washed out by the band electrons doped by V_O



Electrostatic repulsion between V_O and formation of pairs



pair binding energy



Boltzmann factor $\exp(E_b / k_B T)$
at 400 K = 10^5 !
all V_O paired at 400 K
P1 could not be observed