Defect studies in $BaTiO_3$ ceramics using positron annihilation spectroscopy

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Introduction

- $BaTiO_3$ (BT): high dielectric constant (up to 12000), positive temperature coefficient of resistivity in n-type BT [1]
- defects have strong influence on properties:

→ dominant native point defects should be vacancies [2,3]:
  - acceptor-type : V_{Ba} and V_{Ti}
  - donor-type : V_O

→ grain boundaries (possible positron traps - increased density of crystal defects)

Previous results

- early work: POLIS is sensitive to V_{Ba} [4], supported by measurements on samples with varying stoichiometry [5]
- V_{Ba} are predominant for La-doping level < 0.5 mol%, for La doping > 0.5 mol% V_{Ti} is the most common avcancy defect [3]
- calculated positron lifetimes [6]:

τ(bulk)= 152 ps, $\tau(V_{Ba})$= 293ps, $\tau(V_O)$=162 ps, $\tau(V_{Ti})$= 204ps.

Objectives

- investiagtion of positron trapping as a function of temperature was not reported before → investigations as a function of temperature
- address defect types by suitable experiments (dependences on doping and annealing)
- investigate effect of grain size on positron trapping

Experimental

Sample preparation:

- production of BT powder by the mixed-oxide method [7]
  - $BaCO_3 + TiO_2 (+La_2O_3)$ $(+SnO_2)$
  - mixing and milling for 24 h
  - calcinating at 1100°C for 2 h
  - fine milling for 24 h
- commercial BT powder was used for high purity samples (for annealing experiments under variable O_2 pressure)
- BT powder was pressed into disks
- Sintering at: 1400°C (coarse grained samples). 1280°C (fine grained samples).

Positron lifetime spectroscopy

- Fast-fast coincidence system, resolution 230 ps (FWHM)
- Positron source : ^{22}NaCl covered with Al-foil.

Temperature dependent measurements

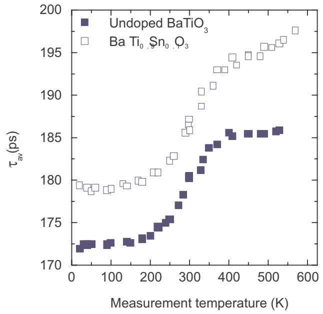

Fig. 1: τ_{av} vs .T in undoped $BaTiO_3$ and $BaTi_{0.9}Sn_{0.1}O_3$

- measured τ_{av} is larger than calculated bulk lifetime (152 ps) [6]

→ **positron trapping at vacancy defects**

Distinct temperature dependence of τ_{av} - why ?

Shallow traps:	improbable, high dielectric constant screens the coulombic interaction
Phase transition:	phase transition at ~400 K in undoped BT can be ruled out because phase transition is shifted to ~300 K in $BaTi_{0.9}Sn_{0.1}O_3$ [8]
Thermal expansion:	can be ruled out, lattice constant increases only slightly with temperature [8]

Probable explanation:
Complex interplay between trapping at different defect types
but not yet well understood

References

[1] R. C. Buchanan, *Ceramic materials for electronics*, Marcel Dekker INC., New York, 1986.
[2] N.S. Hari, T.R.N. Kutty, J. Mat. Sci. 33 (1998), p. 3275.
[3] H. M. Chan, M. P. Harmer and D. M. Smyth, J. Am. Cer. Soc. 69 (1986), p. 507.
[4] N. Tsuda et al., *Proc. 5th Int. Conf. on Positron annihilation* (1979), p. 479.
[5] C. Q. Tang, Cryst. Res. Technol. 29 (1994), p. 865.
[6] V. J.Ghosh and B. Nielsen, Phys. Rev. B 61 (2000), p. 201.
[7] H.T. Langhammer, A. Polity, K.-H. Felgner, H.-P. Abicht, *Proc. Conf. Electroceramic V, Aveiro, Portugal* (1996), part 2 p. 48.
[8] Landolt-Börnstein, *Numerical data and functional relationships in science and technology*, Vol. 16, *Ferroelectric and related substances*, *Oxides,* Springer, Berlin, 1981.
[9] C. Hübner, T. Staab, R. Krause-Rehberg, Appl. Phys. A 61 (1995), p. 203.

Annealing under variable oxygen pressure

- spectra decomposition failed in most cases

→ defect identification with POLIS not possible
→ annealing under variable oxygen pressure (pO_2) to change defect concentration in a well defined way

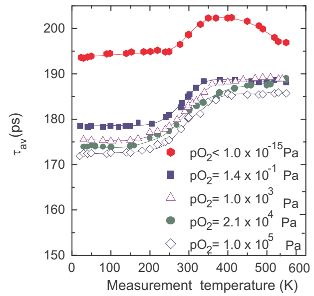

Fig. 2: τ_{av} vs. T in undoped BT annealed under various oxygen pressures as indicated. Annealing was done at 1200°C for 2h.

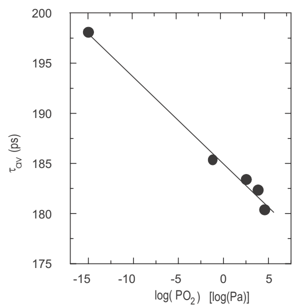

Fig. 3: τ_{av} at 300 K in undoped BT as a function of log pO_2

- increase of τ_{av} with pO_2 indicates positron trapping at V_O
- but measured τ_{av} is higher than 162 ps (calculated for V_O [6])
- higher lifetime of 293 ps was calculated for V_{Ba} [6]

→ **Neutral complex V_{Ba}''–$V_O^{\bullet\bullet}$ is the most probable defect**

Effect of grain size on positron trapping

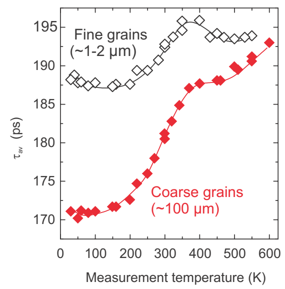

Fig. 4: τ_{av} vs. T in undoped BT with different grain size.

- Grain size 1 µm: ~ 30 % of all positrons can reach the grain surface [9]
- Grain size 100 µm: fraction of positrons reaching the surface is negligible [9]

→ **no influence of grain boundaries on positron trapping in coarse grained samples** (all other in the present work)

Vacancies in donor (La) doped $BaTiO_3$

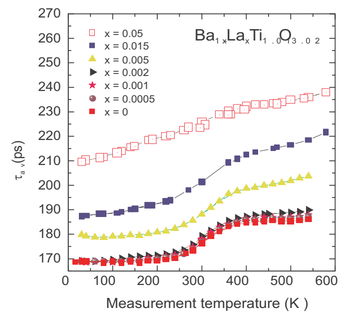

Fig. 5: τ_{av} vs. T in La-doped BT . The La contents are indicated in the figure.

$[La_{Ba}^{\bullet}] + p = 2[V_{Ba}''] + 4\,[V_{Ti}''''] + n$

→ donor doping enhances formation of acceptor-type vacancies

→ positrons are trapped at V_{Ba} or V_{Ti}

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