Analysis of structural characteristics in doped $BaTiO_3$ ceramics

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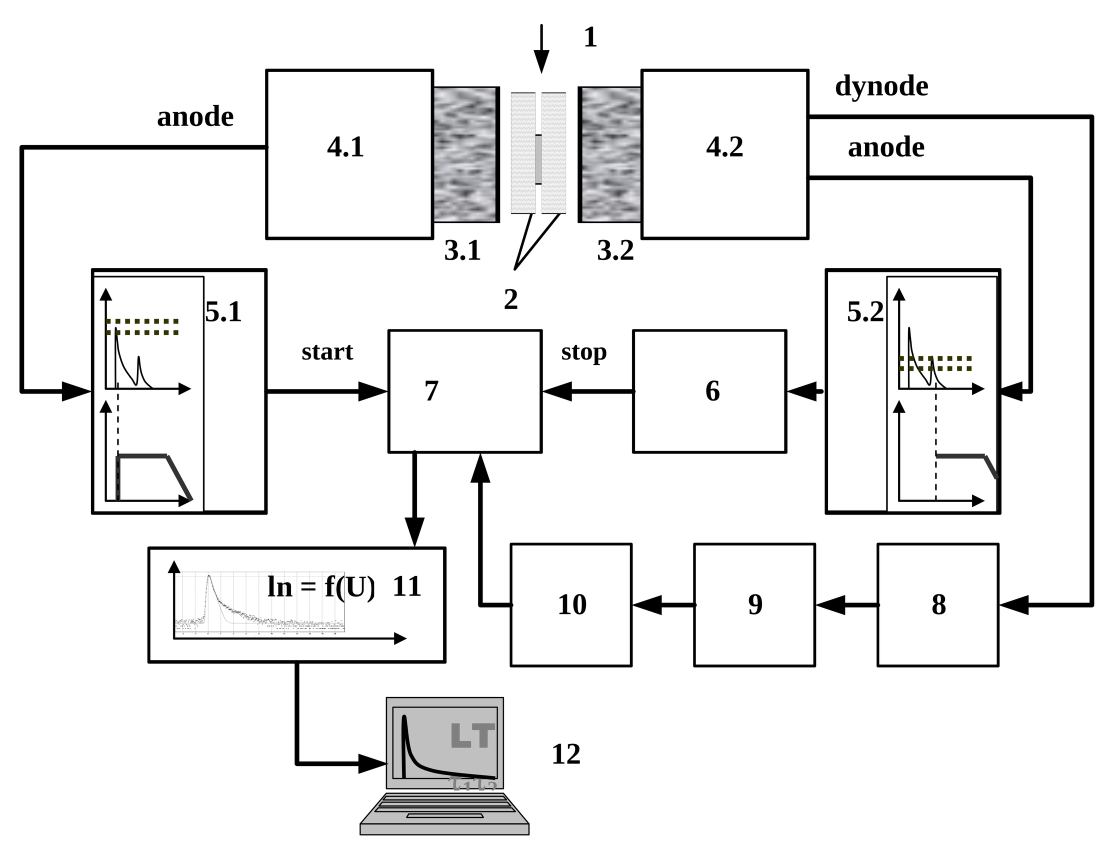
Introduction

In this work inner-structure properties in undoped and Y-doped $BaTiO_3$ ceramics were studied using combined methods. BaTiO3 ceramics doped with 0.2, 0.4, 0.6 and 0.8 mol% of Y were sintered at 1250 °C. The positron annihilation lifetime (PAL) measurements were performed with an ORTEC spectrometer using ^{22}Na source placed between two sandwiched ceramic samples. The obtained data were treated with LT computer program, the best results were obtained to two-component fitting procedures.

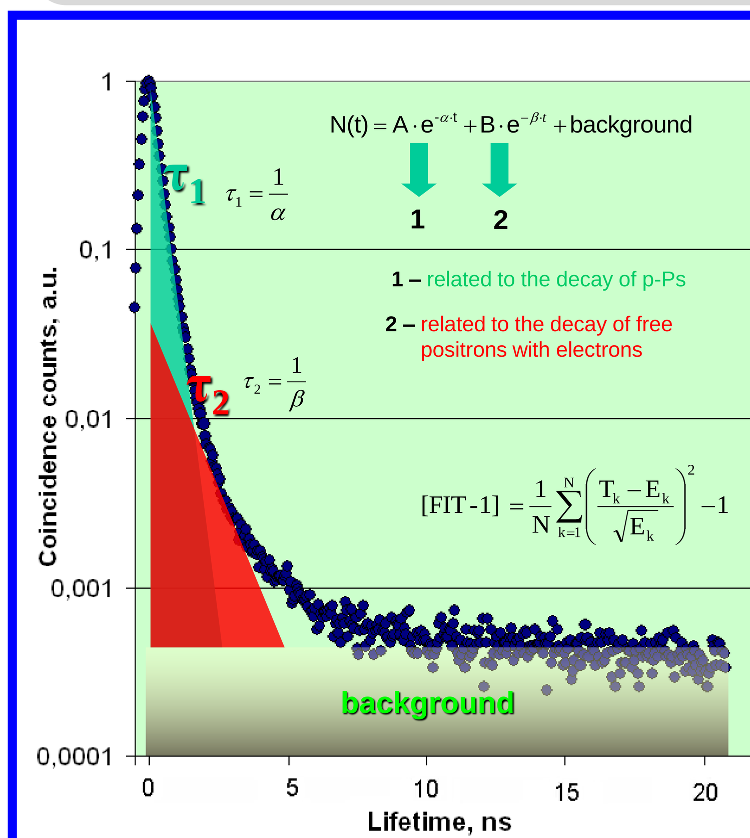
EXPERIMENTAL: Positron Annihilation Lifetime (PAL) Spectroscopy



Block-scheme of conventional sample-source "sandwich" arrangement for PAL measurements using the ORTEC apparatus:

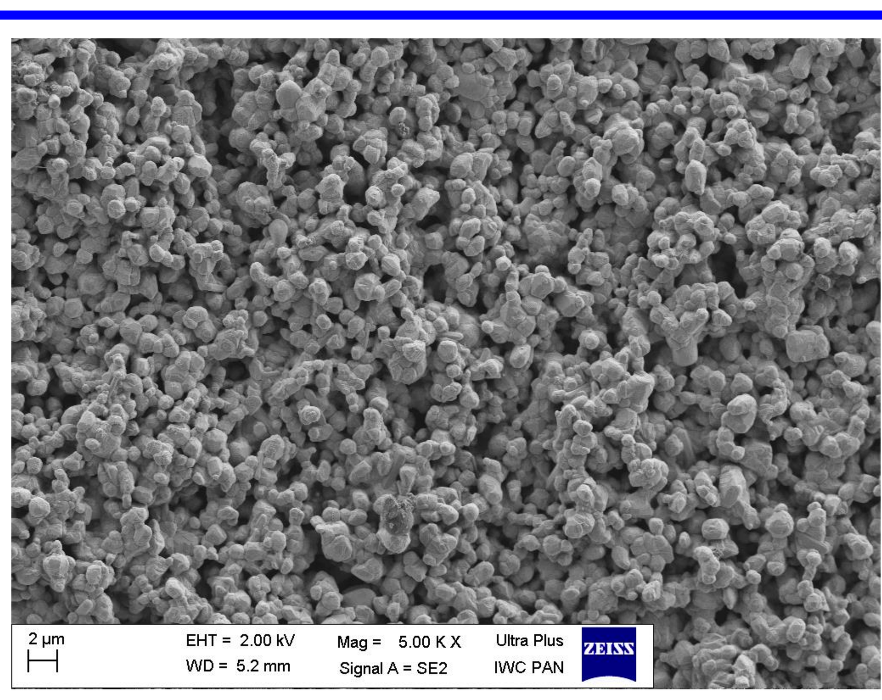
1 – foil-covered ^{22}Na source,
2 – two identical samples,
3.1 and 3.2 – scintillators of γ-quanta,
4.1 and 4.2 – photomultipliers,
5.1 and 5.2 – constant fraction discriminators,
6 – delay line,
7 – time-pulse height converter,
8 – preamplifier,
9 – amplifier,
10 – single channel analyzer,
11 – multichannel analyzer,
12 – personal computer.

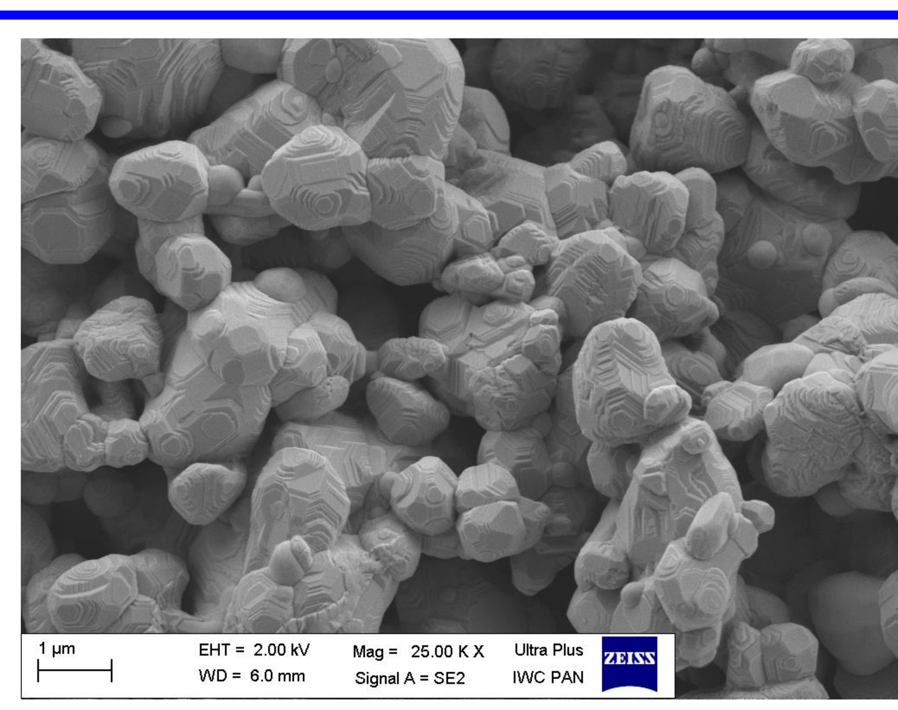
MATHEMATICAL TREATMENT of PAL DATA: LT computer program, 2-component fitting procedure



$\tau_{av.} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}$	**Mean positron lifetime:** reflects cumulative defect environment prevailing in sample
Lifetime τ_b: associated with the positron trapping in defect-free bulk	$\tau_b = \frac{I_1 + I_2}{\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2}}$
$\kappa_d = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_2}\right)$	**Positron trapping rate in defects**
$\tau_2 - \tau_b$	Size measure of extended defects where positrons are trapped
Represents the nature of defects	τ_2/τ_b

Typical microstructure of ceramics



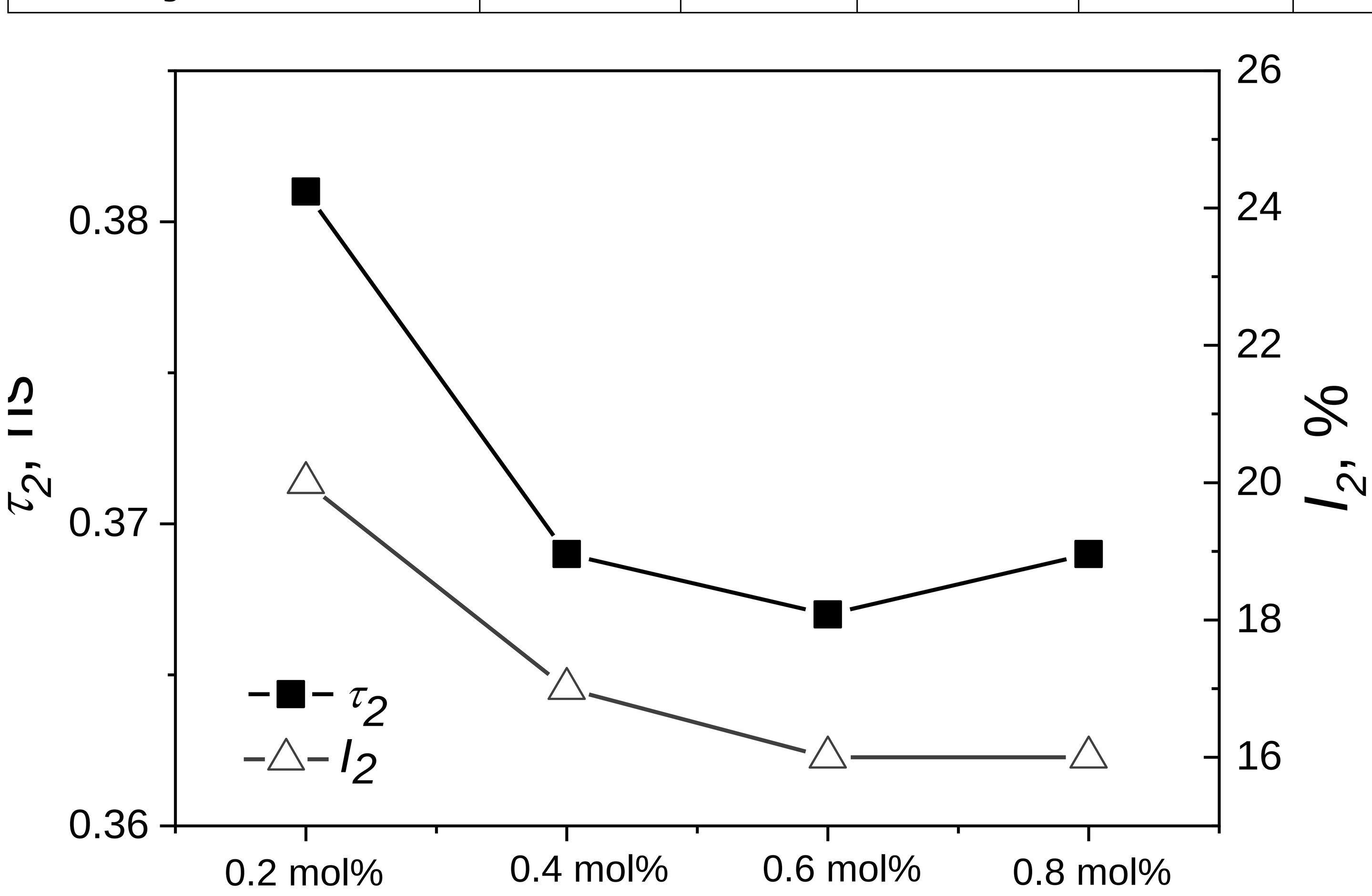


Undoped $BaTiO_3$ ceramics and doped with 5, 10 and 15 mol% of Ca were sintered at 1250 °C. The PAL measurements were performed with an ORTEC spectrometer using ^{2}2Na source placed between two sandwiched ceramic samples. The obtained data were treated with LT computer program, the best results corresponding to two-component fitting procedures. The numerical values of trapping parameters (positron lifetime in defect-free bulk τb, average positron lifetime τav. and positron trapping rate of defect κd) were calculated using short and long positron-trapping lifetimes τ_1 and τ_2, as well as component intensities I_1 and I_2 ($I_1 + I_2 = 1$). The difference (τ_2 - τ_b) can be accepted as a size measure of extended defects where positrons are trapped, the τ_2/τ_b ratio represents the nature of these defects.

RESULTS: PAL characteristics

Sample	Fitting parameters				Components input	
	τ_1, ns	I_1, a.u.	τ_2, ns	I_2, a.u.	$\tau_{av.}^{1}$, ns	$\tau_{av.}^{2}$, ns
$BaTiO_3$	0.151	0.78	0.315	0.22	0.12	0.07
$BaTiO_3$ + 0.2 mol% Y	0.160	0.80	0.381	0.20	0.13	0.08
$BaTiO_3$ + 0.4 mol% Y	0.159	0.83	0.369	0.17	0.13	0.06
$BaTiO_3$ + 0.6 mol% Y	0.160	0.84	0.367	0.16	0.13	0.06
$BaTiO_3$ + 0.8 mol% Y	0.161	0.85	0.369	0.15	0.14	0.06

Sample	Positron trapping modes				
	$\tau_{av.}$, ns	τ_b, ns	κ_d, ns^{-1}	$\tau_2 - \tau_b$, ns	τ_2/τ_b
$BaTiO_3$	0.187	0.170	0.76	0.14	1.85
$BaTiO_3$ + 0.2 mol% Y	0.205	0.181	0.75	0.20	2.11
$BaTiO_3$ + 0.4 mol% Y	0.194	0.175	0.59	0.19	2.10
$BaTiO_3$ + 0.6 mol% Y	0.193	0.176	0.57	0.19	2.09
$BaTiO_3$ + 0.8 mol% Y	0.193	0.176	0.53	0.19	2.09



In respect to SEM investigations, typical ceramic samples show grain-porous microstructure and assemblies of fractional grains. By accepting two-state positron trapping model, for polycrystalline ceramic materials the short lifetime of τ_1~0.16 ns is generally attributed to the free annihilation of positrons. This value also correlated with theoretically calculated free positron lifetime in $BaTiO_3$. The obtained value is closed to $BaTiO_3$ single crystal. The presently observed values of τ_2~0.37 ns which is believed to come from the annihilation of positrons at vacancy complexes formed between the oxygen vacancies and the metal ion vacancies. It is shown that τ_2 decreases with rise of Y amount in $BaTiO_3$ ceramics from 0.2 to 0.6 mol% and increases in samples with 0.8 mol% of Y the intensity I_2 decreases from 20 to 15 %.

This indicates that doping of Y results in decreasing of the size of free-volume defects in ceramics and decreasing of their amount. So, process of so-called shrinking of defects is take place at posing of $BaTiO_3$ ceramics by Y in amount of 0.4 and 0.6 mol%, while future increasing the Y content to 0.8 mol% leads to weakly expressed agglomeration of free-volume defects.