Analysis of structural properties of Ca-doped $BaTiO_3$ ceramics

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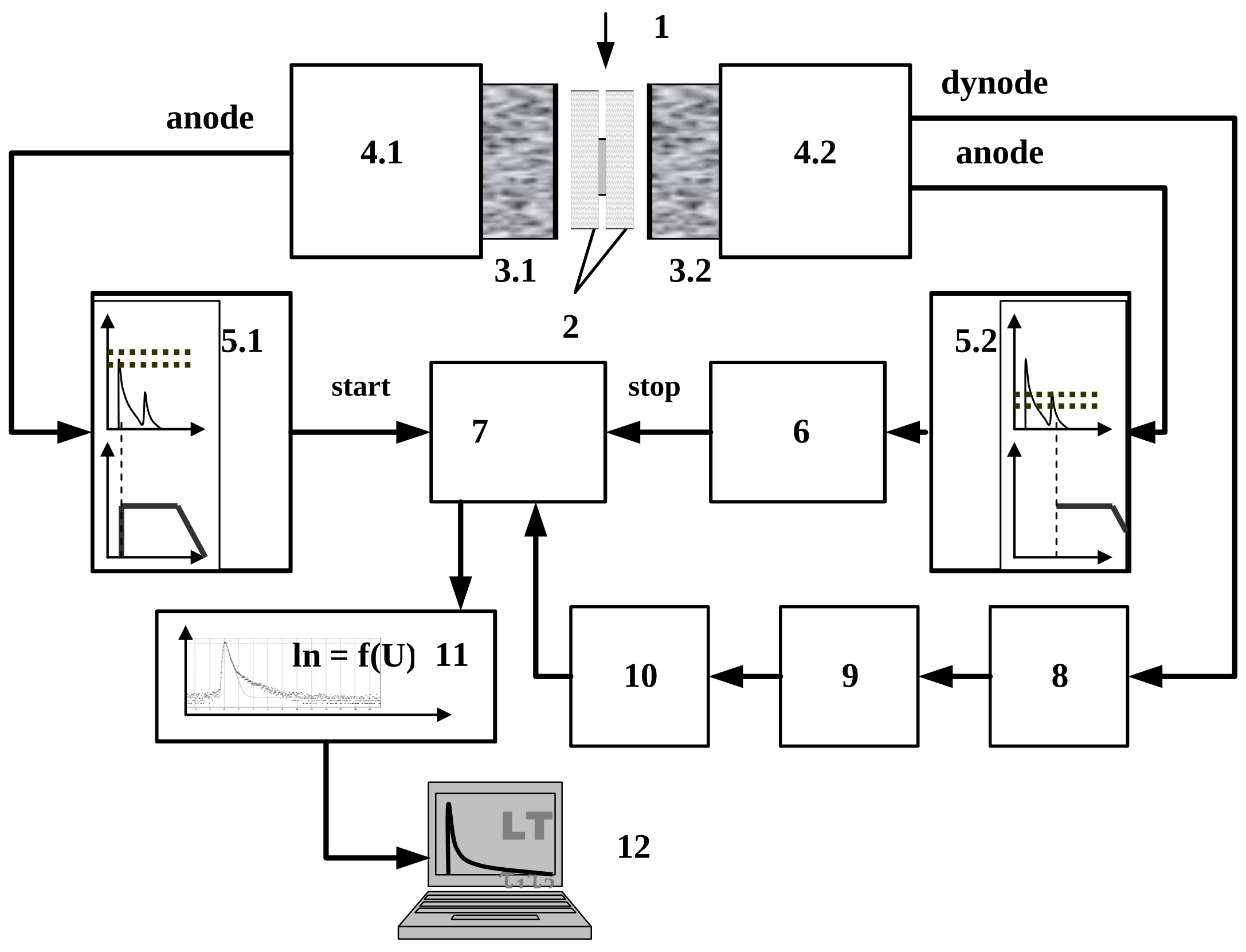
Introduction

Barium titanate (BaTiO3) is a displacement-type ferroelectric perovskite, widely studied for its basic properties and extensive applications [1]. In this materials defects originated by the preparation method. The aim of this work is study of free-volume defects in undoped and Ca-doped $BaTiO_3$ ceramics using positron annihilation lifetime (PAL) spectroscopy in comparison with scanning electron microscopy (SEM) method.

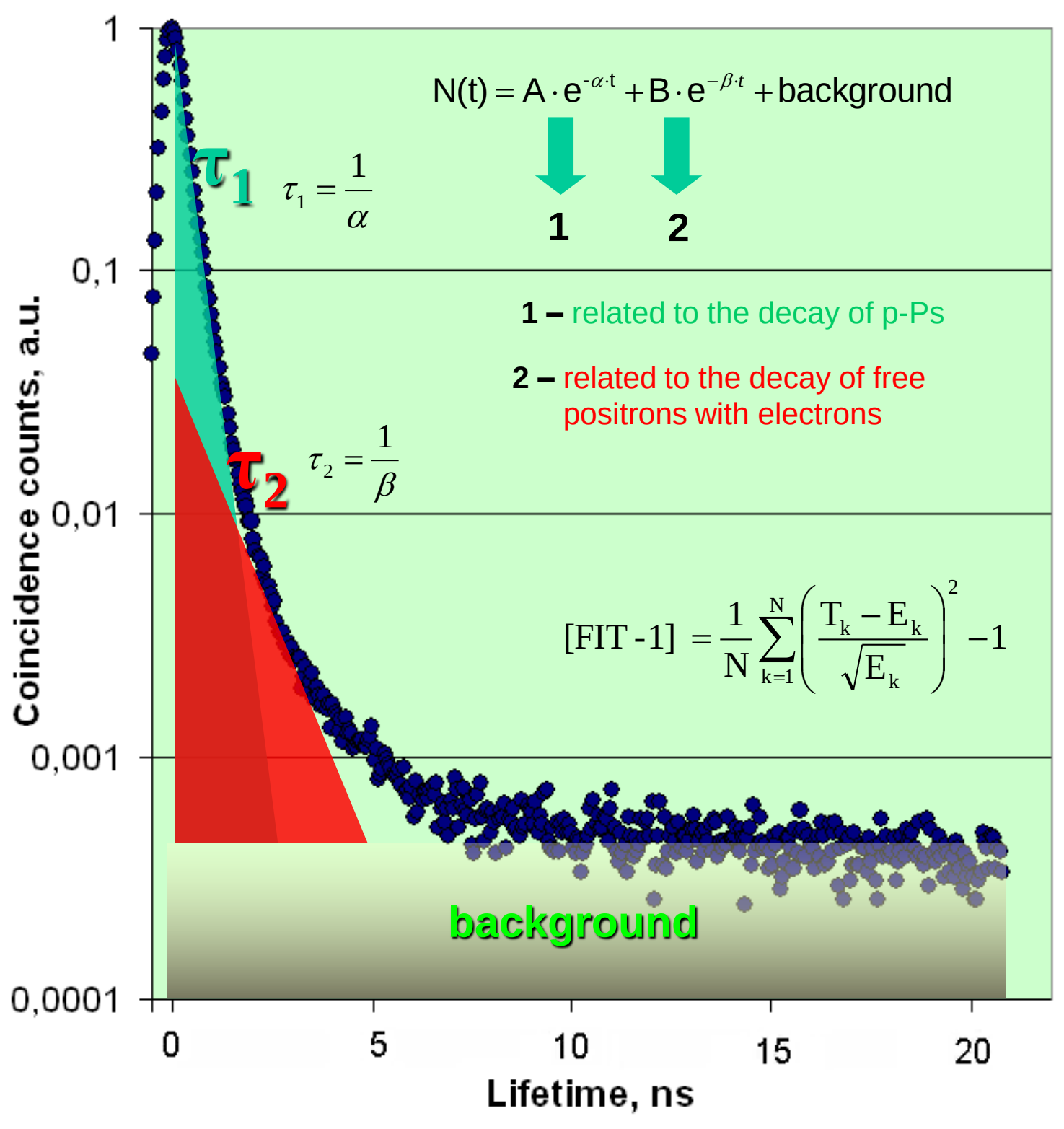
EXPERIMENTAL:
Positron Annihilation Lifetime (PAL) Spectroscopy



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

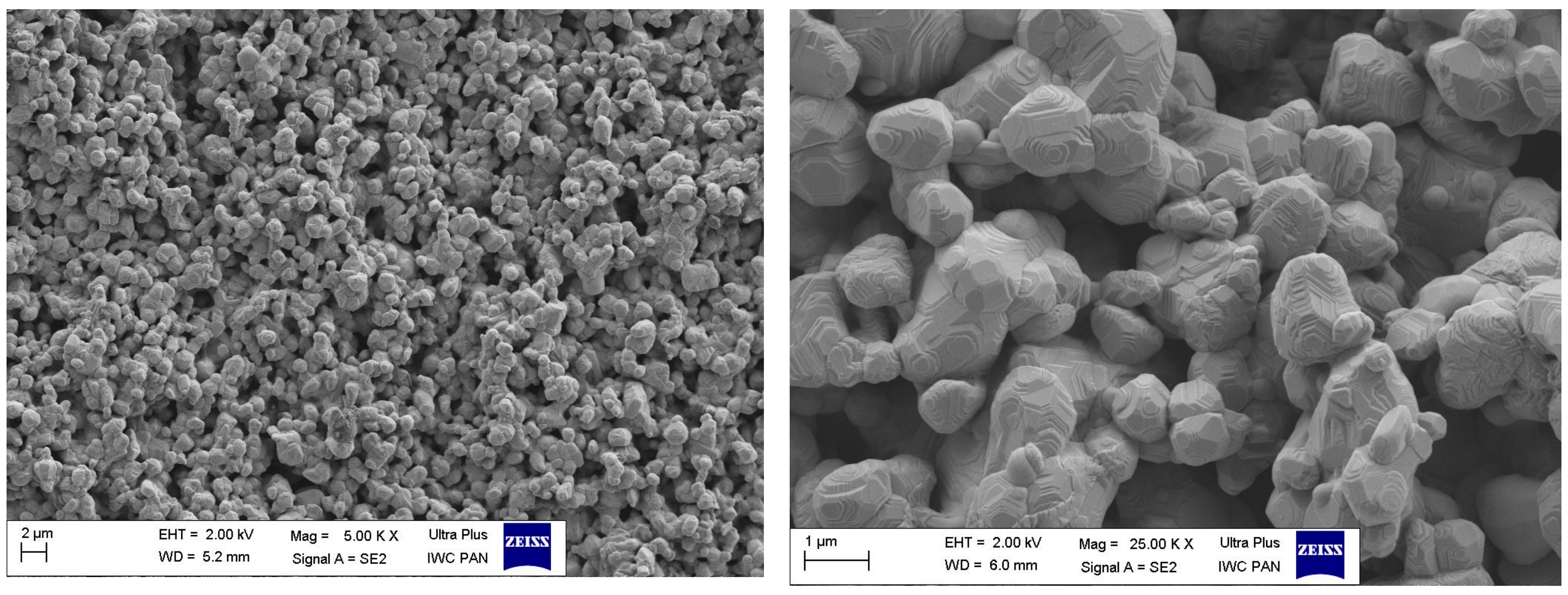
1 – foil-covered ^{22}Na source,
2 – two identical samples,
3.1 and 3.2 – scintillators of γ-quanta,
4.1 and 4.2 – photomultipliers,
5.1 and 5.2 – constant fraction discriminators,
6 – delay line,
7 – time-pulse height converter,
8 – preamplifier,
9 – amplifier,
10 – single channel analyzer,
11 – multichannel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

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



$\tau_{av.} = \dfrac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}$	**Mean positron lifetime:** reflects cumulative defect environment prevailing in sample
Lifetime τ_{b}: associated with the positron trapping in defect-free bulk	$\tau_b = \dfrac{I_1 + I_2}{\dfrac{I_1}{\tau_1} + \dfrac{I_2}{\tau_2}}$
$\kappa_d = \dfrac{I_2}{I_1}\left(\dfrac{1}{\tau_b} - \dfrac{1}{\tau_2}\right)$	**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

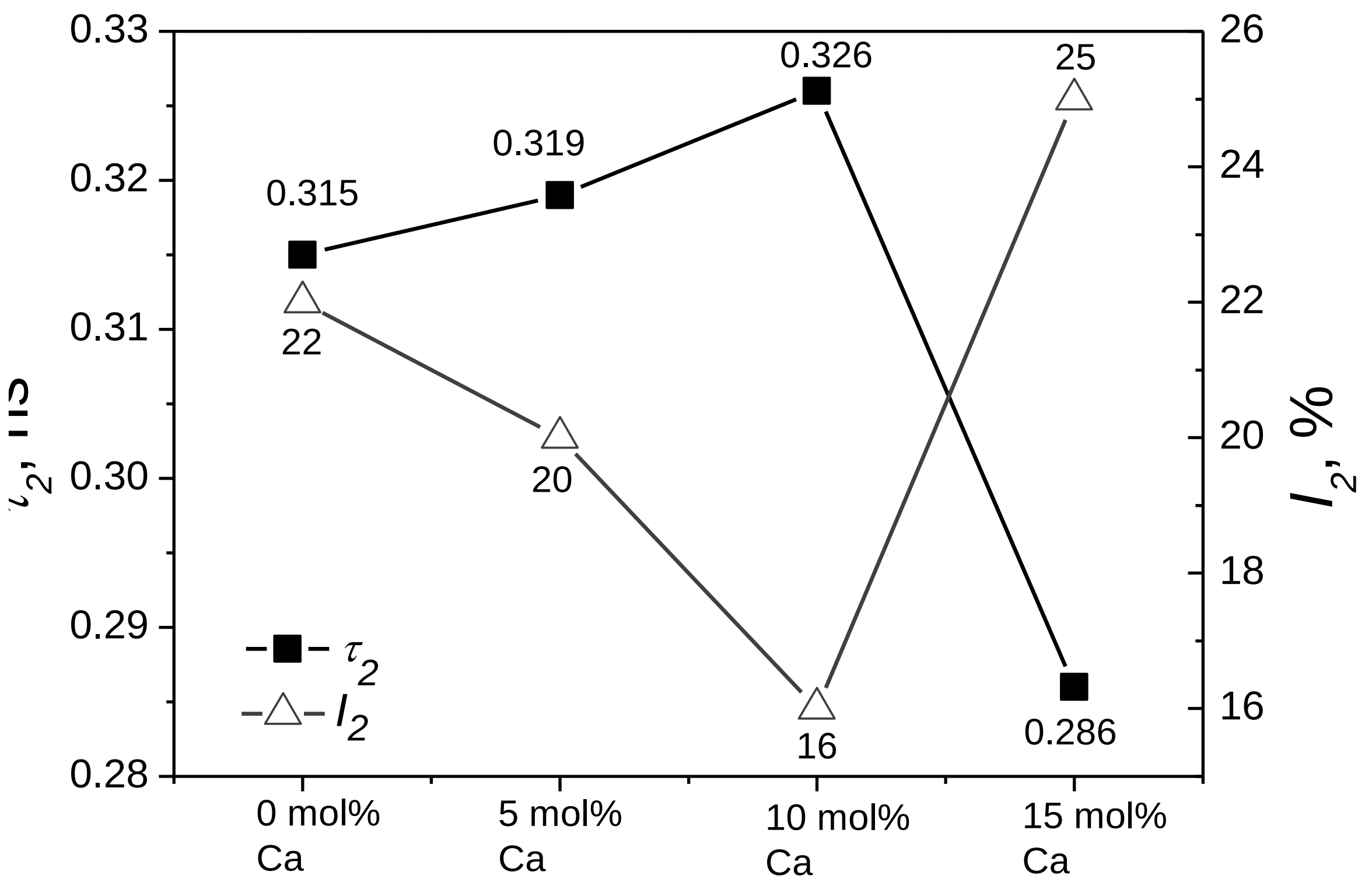


Undoped $BaTiO_3$ ceramics and doped with 5, 10 and 15 mol% of Ca were sintered at 1250 °C. The PAL measurements were performed with an ORTEC spectrometer using 22Na source placed between two sandwiched ceramic samples. The obtained data were treated with LT computer program, the best results corresponding 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 ($\tau_2 - \tau_b$) 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
$BaTiO_3$ + 5 mol% Ca	0.152	0.80	0.319	0.20	0.12	0.06
$BaTiO_3$ + 10 mol% Ca	0.155	0.84	0.324	0.16	0.13	0.05
$BaTiO_3$ + 15 mol% Ca	0.143	0.75	0.286	0.25	0.11	0.07

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
$BaTiO_3$ + 5 mol% Ca	0.185	0.170	0.69	0.15	1.88
$BaTiO_3$ + 10 mol% Ca	0.183	0.169	0.56	0.16	1.93
$BaTiO_3$ + 15 mol% Ca	0.178	0.163	0.86	0.12	1.76



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_1~0.15 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 second lifetime τ_2 arises from annihilation of positrons at defect sites. The presently observed values of τ_2~0.32 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 obvious from Figure that τ_2 increases with rise of Ca amount in $BaTiO_3$ ceramics from 5 to 10 mol% and decreases in samples with 15 mol% of Ca. the intensity I_2 decreases from 22 to 16 % and increases to 25 % in samples with 15 mol% of Ca.

This indicates that doping of Ca results in increasing of the size of free-volume defects in ceramics and decreasing of their amount. So, process of agglomeration of defects is take place at posing of $BaTiO_3$ ceramics By Ca in amount of 5 and 10 mol%, while future increasing the Ca content to 15 mol% leads to fragmentation of free-volume defects.