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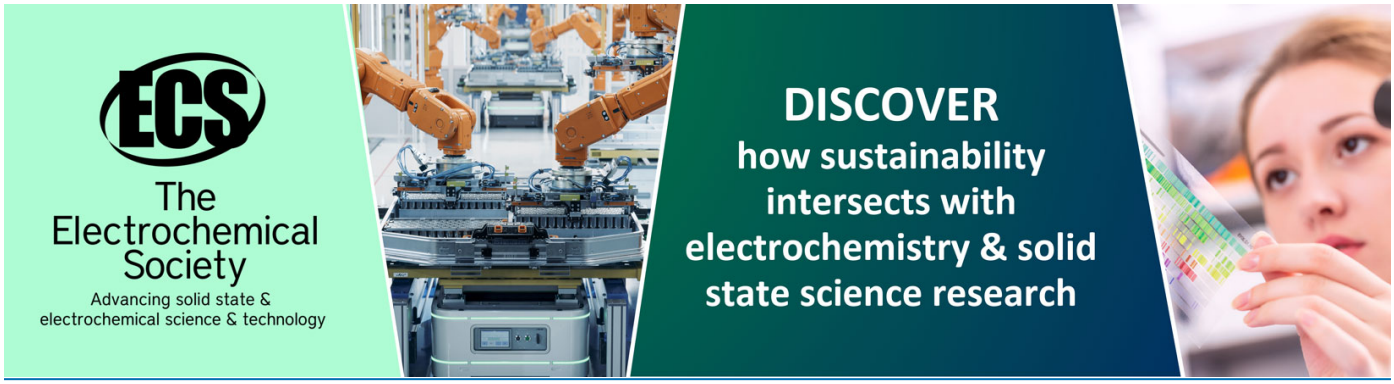

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Systematics of positron lifetime spectroscopy measurements in ferroelectrics

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Abstract. In the paper is demonstrated the use of positron lifetime spectroscopy (PLS) in a comparative study of the results in ferroelectrics. The first part is devoted to the application of PLS as a probe for measurements of ferroelectrics. In Triglycine Sulphate (TGS) $(NH_3CH_2COOH)_3H_2SO_4$, Rochelle Salt (RS) $NaKC_4H_4O_64H_2O$ and Potassium Dihydrogen Phosphate (KDP) KH_2PO_4 at different temperatures and gamma irradiation doses is established the existence of three positron lifetime components. This experimental results show that the second long lifetime component as a function of temperature in order-disorder ferroelectrics TGS, RS and KDP is due to the positron trapping in negatively charge defects of ferroelectric. The positron spectroscopy method is effective for measurements of extremely small defects and voids, which is important for the next exploitation period of the ferroelectrics. PLS measurements of ferroelectrics show that about the third lifetime component is due to the local formation of orhto-positronium state on the boundary between the domains. In the second part the PLS analysis has been applied for examination the electronic and defect structure in selected ferroelectrics materials. In gamma irradiated TGS positrons are trapped in the defect states of the oxygen ions of the two radicals CH_2COO^- and NH_3CHCOO^-. In RS positrons are trapped also in the defect states of the oxygen ions and OH groups.

1. Introduction

Positron lifetime spectroscopy (PLS) is a non-destructive technique for detection of open-volume defects in materials (from single vacancies to nano-voids) [1-3]. Positron spectroscopy measuring of the orhto-positronium (o-Ps) and para-positronium (p-Ps) lifetime relates to the free-volume size distribution in the samples. A positron injected into ferroelectrics material during its thermalization process may bound with an electron to from Ps, which is a hydrogen-like ''atomic'' state. The spin orientation, which governs the annihilation rate, leads to drastically different p-Ps and o-Ps lifetimes in vacuum, 0.125 ns and 142 ns, respectively [4]. Para-Ps and ortho- Ps undergo the process of pick-off annihilation with surrounding electrons. Studies of the ferroelectric materials show that the triplet ortho-Ps state depends on domain structure and spontaneous polarization [5]. The simple model describing positron interaction in ferroelectrics is based on the atomic polarizability on the crystal [6, 7]. In some ferroelectrics [8, 9] a correlation has been observed between the increase of the positron long lifetime component and the temperature. The positive positron charge open the possibility for determing the charges in charge states in technologically important order-disorder ferroelectrics.
Conducting ferroelectrics have been a subject of substantial research interest recently due to their real and potential application in modern technologies as computer memories, sensitive infrared detectors, for laser frequency conversion ($KTiOPO_4$) [10-13] and fusion materials ($BaTiO_3$). Ferroelectric

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ceramics are important electronic materials that have a wide range of industrial and commercial applications, such as piezoelectric sonar or ultrasonic transducers, medical diagnostic transducers, high-dielectric constant capacitors, pyroelectric security sensors, electro-optical light valves, and ultrasonic motors. Barium titanate ($BaTiO_3$) which is a good candidate for a variety of applications, such as piezoelectric actuators, multiplayer ceramic capacitors and positive temperature coefficient resistors, due to its excellent dielectric, ferroelectric and piezoelectric properties. The perovskite family having a structure of the type ABO_3 is the most popular type of ferroelectrics. Many ferroelectric materials such as: lead titanate, barium titanate, lead zirconate titanate, lead lanthanum zirconate titanate, and relaxor ferroelectrics like lead magnesium niobate have this perovskite type structure. In future different positron sources for investigation the structure of new materials will be produced by using the new Cyclotron at the Institute for Nuclear Research and Nuclear Energy (INRNE) [14].

1.1. Experimental method

The positron lifetimes spectroscopy measurements were carried out with a conventional fast–fast ORTEC gamma spectrometer, with Phillips XP2020 photomultiplier tubes. ^{22}NaCl deposited on Kapton foil as a positron source was used. The β^+ decay of ^{22}Na is followed by an ‘‘instantaneous’’ emission of a ~1.3 MeV photon, which is used to start the experimental clock, whereas a stop signal is provided by the detection of one of the annihilation photons. A sealed-in Kapton foil ^{22}NaCl source with $1.1x10^6$ Bq activity was sandwiched between two pieces of each sample. The count rate was optimized at the expense of timing resolution (FWHM = 240 ps Full Width at Half Maximum,). All spectra were collected with 10^6 counts. The source correction was the lifetime component of 384.5 ps with intensity of 5.75%. The spectra were analyzed using the well-known PATFIT computer program, decomposes the spectrum into three discrete lifetime components. Gamma irradiation of the samples was employed with a ^{60}Co gamma source facility at an exposure dose rate of $1.26x10^4$ Roentgen/hr. All the measurements were performed in the (001) plane of TGS. The Rochelle salt samples were cut along the (100) axis. KDP samples were cut parallel to the c-axis.

2. Results and discussion

The experimental positron lifetime spectra of Triglycine Sulphate (TGS) $(NH_3CH_2COOH)_3H_2SO_4$, Rochelle Salt (RS) $NaKC_4H_4O_64H_2O$ and Potassium Dihydrogen Phosphate (KDP) KH_2PO_4 were decomposed into three components. The positron parameters are plotted in Figures 1-2. The lifetime of trapped positron σ_2 at defect states shown in Figure 1 a,b,c, increases in TGS, RS and KDP with increasing of temperature. The higher intensity shows that defect states in ferroelectrics increase with temperature. During the changes of the spontaneous polarization with temperature in ferroelectrics are formed local regions, in which domains are polarized in different directions due to the rearrangement in the dipole polarity. With increasing of temperature in domains are formed dipole charge states, which play the role of point defects. They are trapping centers for positrons. In this study the positron interaction in order-disorder ferroelectrics is considered in terms of commonly accepted ionic models. The variation of σ_2 and I_2 in gamma-irradiated TGS and RS is shown in Figure 2 a,b. The interpretation of our experimental data shows that in gamma irradiated TGS positrons are trapped in defect states of the oxygen ions of the two radicals CH_2COO^- and NH_3CHCOO^-. The greater part of the positrons, which give a contribution to σ_2 lifetime component in RS, annihilate also in the defect states of the oxygen ions and OH^- groups. On the other side water molecules in RS have a permanent dipole moment. In addition positron cannot form bound state with hydrogen [15], so the positron interaction in ferroelectrics is carried out mainly through attraction or positrons from the negative charge defect states of oxygen ions. In gamma irradiated TGS the irradiation breaks the hydrogen bonds and two Glycine groups are formed [16]. The defect producing mechanism of gamma-irradiation in ferroelectrics is not by atomic displacement but by ionization resulting in molecular rearrangements. In the studied ferroelectric crystals TGS, RS and KDP, the existence of third lifetime

component is due to the positronium formation. The analysis of the positron lifetime spectra shows that ortho-positronium state is formed on the boundary between the domains [17].

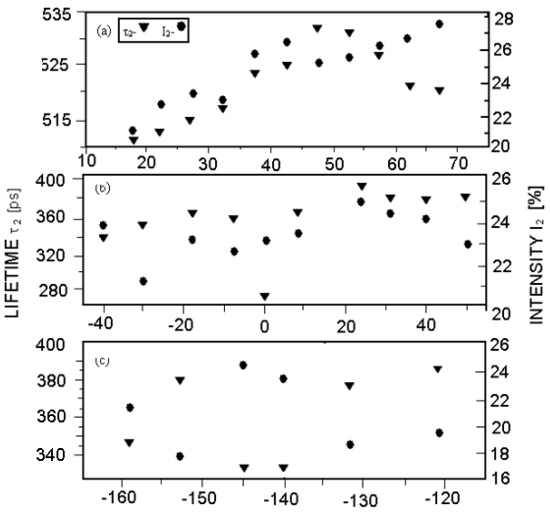

Figure 1. Positron lifetime components and its intensity as a function of temperature (a) TGS, (b) RS, (c) KDP.

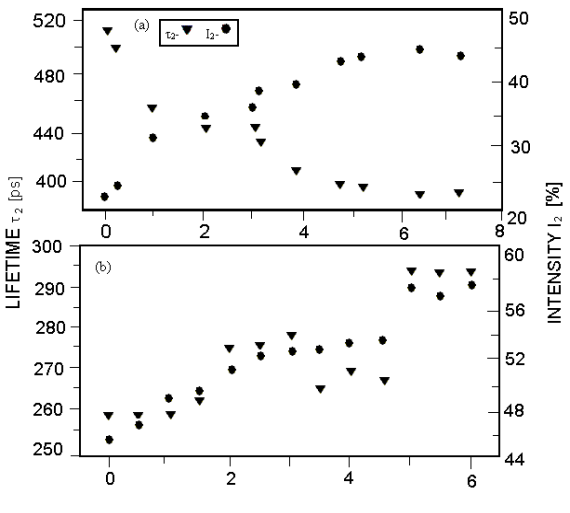

Figure 2. Positron long lifetime components and its intensity as a function of gamma irradiation dose (a) TGS, (b) RS.

D. J. Keeble et. al. reported positron annihilation lifetime spectroscopy measurements identify A- and B-site cation vacancies in ferroelectric perovskite oxides (ABO_3). The experimental results for two pairs of crystal $PbTiO_3$ and undoped and Fe doped ceramic lead zirconium titanate $Pb(ZrTi)O_3$ (PZT) are shown in table 1. Positron trapping to B-site vacancies was inferred in PZT. Temperature dependent studies showed that the defect specific trapping rate was higher for V_B compared to V_{Pb}, consistent with the larger negative charge. Doping PZT with Fe increased the fraction positron trapping to V_B compared to V_{Pb}-type defects [18].

Table 1. Experimental positron lifetime values (ps) for $PbTiO_3$ and PZT [18].

Samples		τ_1 (ps)	τ_2 (ps)	$\tau_{average}$ (ps)	$\tau_в$ (ps)
$PbTiO_3$ crystals	P1crystals	159.0	280	170	165
	P2 crystals	139.5	285	191	170
$Pb(ZrTi)O_3$ ceramic	undoped	185	281	239	
	0.1%Fe	186	284	230	
	0.5%Fe	193	293	225	
	1.0%Fe	198	290	211	

The experimental results by R.A. Mackieet. et. al. shows in table 2. PALS experiments on undoped, electron irradiated, and Nb doped $SrTiO_3$ single crystals from several different suppliers are presented. The Sr vacancy defect related positron lifetime was obtained from measurements on Nb doped, electron irradiated, and vacuum annealed samples. Undoped crystals showed a defect lifetime component dominated by trapping to Ti vacancy related defects [19].

Table 2. Experimental positron lifetime values (ps) for $SrTi\,O_3$ samples, they are single crystal unless state, either undoped (UD), Nb-doped, or electron irradiated (dose $3x10^{18}$ e^-cm^{-2}) [19].

Samples		τ_1 (ps)	τ_2 (ps)	I_2 (%)	$\tau_{average}$ (ps)	$\tau_в$ (ps)
$SrTiO_3$ single crystals	UD	130.6	201.3	41.2	160	153
	UD	123.5	201.3	54.3		156
	UD	120.0	205.8	55.6		156
	UD	94.4	198.5	77.9		159
	UD	128.3	222.4	42.6		156
	Nb	130.6	272.4	23.4		149
	e^-	166.3	260.7	20.9		180
$SrTiO_3$ ceramic	UD	176.3	276.3	6.2		180

Table 3. Positron lifetime results for $Bi_7Fe_{2.75}Co_{0.25}Ti_3O_{21}$ (BFCTO) ceramic [20].

Samples	τ_1 (ps)	τ_2 (ps)	I_2 (%)	τ_m (ps)
BFCTO $Bi_7Fe_{2.75}Co_{0.25}Ti_3O_{21}$ (BFCTO) ceramic	233	427.7	26.57	284.7
BFCTO-500	239.9	447.5	15.42	271.9
BFCTO-650	227	415.2	14.08	253.5
BFCTO-800	218	408.8	9.03	232.0

Table 4. Positron annihilation lifetime and intensity in free state and defect state, and the calculated average lifetime and bulk lifetime [21].

Sample $KTiOPO_4$	τ_1 (ns)	I_1 (%)	τ_2 (ns)	I_2 (%)	τ_{av} (ns)	$\tau_в$ (ns)
S1-881 ^oC	0.1949	43.43	0.388	53.88	0.2937	0.2765
S3-985 ^oC	0.1948	34.71	0.3879	63.16	0.3126	0.2933
K6-950 ^oC	0.1864	32.8	0.3756	65.8	0.3083	0.2848

W.N. Ge et. al. reported correlation between ferromagnetism and the concentration of interfacial defects in multiferroic $Bi_7Fe_{2.75}Co_{0.25}Ti_3O_{21}$ studied by positron annihilation. Positron annihilation measurements reveal that the interfacial defects disappear obviously when the annealing temperature increased, which is found to agree well with the variation of saturation magnetization. For

convenience, the samples with different annealing temperatures of 500^{o}C, 650^{o}C, 800^{o}C and the non-annealed sample are named as BFCTO-500, BFCTO-650, BFCTO-800 and BFCTO-RT, respectively. Positron lifetime spectra were measured for BFCTO samples annealed at different temperatures. These results reveal useful information about the defect structure of the BFCTO samples. The results are shown in table 3 [20].
Yang Zhang et. al. used positron annihilation spectroscopy (PAS) to study vacancy defects in $KTiOPO_4$ (KTP) single crystals. Positron annihilation lifetime spectroscopy combined with dielectric measurements identified the existence of oxygen vacancies and reflected the concentration of vacancy defects in three samples. The vacancy defects in KTP do not consist of monovacancies, but rather vacancy complexes. However, the gray track effect limits its applications at high laser power.
S1 was grown in the flux of $K_4P_2O_7$ (K_4) and PbO, and the saturation point was about 881^{o}C. S3 was grown in a flux with PbO and excess K^+ ions, and the saturation point was about 985^{o}C. Sample K6 was grown from $K_6P_4O_{13}$ with a saturation point of 950°C. The PAS results show that the potassium vacancy concentration of sample S1 is the lowest, while that of samples S3 and K6 is approximately the same table 4. In summary, we used PAS to measure the cation vacancy concentration and vacancy type in KTP [21]**.**

3. Conclusions

In TGS, RS and KDP at different temperature and gamma irradiation doses is established the existence of three positron lifetime components. These experimental results show that the second long lifetime component as a function of temperature in order-disorder ferroelectrics TGS, RS and KDP is due to the positron trapping in negatively charge defects of ferroelectrics. In gamma irradiated TGS positrons are trapped in the defect states of the oxygen ions of the two radicals CH_2COO^- and NH_3CHCOO^-. In RS positrons are trapped also in the defect states of the oxygen ions and OH groups. The third lifetime component is due to the local formation of ortho-positronium state on the boundary between the domains.
The PAS was used to measure the cation concentration and vacancy type in KTP. From vacancy open-volume, observe that there are vacancy-complex defects in the crystals.
The effect of annealing on the ferromagnetism and interfacial defects in the BFCTO samples was studied. In the annealing temperature interval between 500^{0}C and 800^{0}C, no phase transition was observed. The interfacial defects evidenced by positrons in the grain boundary region disappear slowly with the increase of annealing temperature. The long lifetime depend on temperature, the concentration of doping Fe atoms and electron irradiation intensity. These results confirm that positron annihilation techniques can characterize vacancy defects in ferroelectrics materials such as: TGS, RS, KDP; perovskite oxide materials ($PbTiO_3$ crystals, $Pb(ZrTi)O_3$ ceramics); $SrTiO_3$ single crystals and $SrTiO_3$ ceramics; $Bi_7Fe_{2.75}Co_{0.25}Ti_3O_{21}$ (BFCTO) ceramic and $KTiOPO_4$ samples.
The long lifetime increases in:
- TGS, RS, KDP, with increasing of temperature;
- $Pb(ZrTi)O_3$ ceramics, with increasing concentration on Fe doping;
- $SrTiO_3$ crystals with, electron irradiated intensity and Nb-dopping concentration. The long lifetime decreases in $Bi_7Fe_{2.75}Co_{0.25}Ti_3O_{21}$ and $KTiOPO_4$.

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