

POSITRON TRAPPING RATE IN SOME  
FERROELECTRICS, SEMICONDUCTORS AND GLASSES

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**Abstract**

This paper presents comparative results of positron spectroscopy studies in ferroelectrics, semiconductors and glasses. The positron lifetime spectroscopy study is focused on the investigation of the positron trapping rate in the ferroelectrics, the Triglycine Sulphate (TGS)  $(\text{NH}_3\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4$ , Rochelle Salt (RS)  $\text{NaKC}_4\text{H}_4\text{O}_6\cdot 4\text{H}_2\text{O}$  and Potassium Dihydrogen Phosphate (KDP)  $\text{KH}_2\text{PO}_4$  structures, semiconductors and glasses. The positive positron charge opens the possibility for determining the changes in charge states in technologically important order-disorder ferroelectrics. The positron lifetime spectroscopy (PLS) results show that the second lifetime component as a function of temperature in order-disorder ferroelectrics TGS, RS and KDP is due to the positron trapping in negatively charged defects of ferroelectric. The PLS analysis has been applied for examination of positron trapping in the electronic-defect structure in selected ferroelectrics materials, semiconductors and glasses.

**Key words:** positron annihilation, positron lifetime, ortho-positronium, gamma-ray spectroscopy, ferroelectrics, spontaneous polarization, semiconductors, glasses

**Introduction.** Positron lifetime spectroscopy (PLS) is well established technique for the study of defects, due to the sensitivity of the annihilation characteristics of the local electron density and to ability of open-volume defects to trap positrons. In particular, (PLS) has been successfully used to study the thermal formation of vacancies in metals and alloys [1,2], recently, in intermetallic [3,4],

while the positron spectroscopy measuring of the o-Ps and p-Ps lifetime relates to the large free-volume sizes distribution in the samples. A positron injected into ferroelectric material after its thermalization process may bound with an electron to form 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 [5], p-Ps and o-Ps undergo the process of pick-off annihilation with surrounding electrons. Studies of the ferroelectric materials show that the triplet o-Ps state depends on domain structure and spontaneous polarization [6]. The simple model describing positron interaction in ferroelectrics is based on the atomic polarizability on the crystal [7,8]. In some ferroelectrics [9,10] a correlation has been observed between the increase of the positron long lifetime component and the temperature. The positive positron charge opens the possibility for determination of the charge states in technologically important order-disorder ferroelectrics. Ferroelectric ceramics as well as semiconductors and glasses are important 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. The positron annihilation methods had a significant impact on defect spectroscopy in solids for identification of vacancies.

PLS method gives highly accurate information for positron trapping rate of positron interaction with electrons. The purpose of the study is to present systematics of positron trapping rate in ferroelectrics, semiconductors and glasses.

**Experimental method.** The positron lifetimes spectroscopy measurements were carried out with a conventional fast-fast ORTEC gamma spectrometer, with Phillips XP2020 photomultiplier tubes.  $^{22}\text{NaCl}$  deposited on Kapton foil as a positron source was used. The  $\beta^+$  decay of  $^{22}\text{Na}$  is followed by an “instantaneous” emission of a  $\sim 1.27$  MeV photon, which is used to start the experimental clock, whereas a stop signal is provided by the detection of one of the 0.511 MeV annihilation photons. A sealed-in Kapton foil  $^{22}\text{NaCl}$  source with  $1.1 \times 10^6$  Bq activity has been sandwiched between two pieces of each sample. The count rate was optimized at the timing resolution (FWHM = 240 ps Full Width at Half Maximum). All spectra have been collected with  $10^6$  counts. The lifetime component of 384.5 ps with intensity of 5.75% is due to source correction. The spectra have been analyzed using the well-known PATFIT computer program which decomposes the spectrum into three discrete lifetime components. In the ferroelectrics gamma irradiation of the samples has been employed with a  $^{60}\text{Co}$  gamma source facility at an exposure dose rate of  $1.26 \times 10^4$  Roentgen/h. All the measurements were performed in the (001) axis of TGS. The Rochelle salt samples were cut along the (100) axis. KDP samples were cut parallel to the *c*-axis.

**Comparison of the results and discussion.** The discussion of the results presented in this section concentrates mainly on identification of the vacancy-type

defects. The experimental positron lifetime spectra of TGS ( $(\text{NH}_3\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4$ ), RS ( $\text{NaKC}_4\text{H}_4\text{O}_6\cdot 4\text{H}_2\text{O}$ ) and KDP ( $\text{KH}_2\text{PO}_4$ ) were decomposed into three components. The correlation between positron trapping rate ( $k$ ) and temperature in TGS, RS and KDP is shown in Table 1a, b, c. Correlation between positron trapping rate and temperature in TGS is shown in Table 1a. The value of positron trapping rate in TGS and RS increases with temperature. The behaviour of  $k$  in KDP shown in Table 1c is different from those in TGS and RS. 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 open defects. They are trapping centres for positrons. In this study the positron interaction in order-disorder ferroelectrics is considered in terms of commonly accepted ionic models. 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  $\text{CH}_2\text{COO}^-$  and  $\text{NH}_3\text{CHCOO}^-$ . The greater part of the positrons, which give a contribution to  $r_2$  lifetime component in RS, annihilate also in the defect states of the oxygen ions and  $\text{OH}^-$  groups. On the other hand, water molecules in RS have a permanent dipole moment. In addition, positron cannot form bound state with hydrogen [11], so the positron interaction in ferroelectrics is carried out mainly through attraction or positrons from the negative charge defect states of oxygen ions.

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 [13].

The value of the positron trapping rate in gamma irradiated TGS and RS shown in Fig. 1, increases with gamma irradiation dose. In gamma irradiated TGS the irradiation breaks the hydrogen bonds and two Glycine groups are formed [12]. The defect producing mechanism of gamma-irradiation in ferroelectrics is not by atomic displacement but by ionization resulting in molecular rearrangements.

Vacancies have been observed at high concentrations in semiconductors and their role in doping and compensation can be quantitatively discussed. Many semiconductors can be grown as thin films, as is the case for GaAs. GEBAUER et al. [14] determined the Gibbs free energy of formation – i.e., the formation enthalpy and entropy – as well as the charge state of Ga vacancies in n-type GaAs by directly probing the vacancy concentration as a function of annealing temperature, arsenic vapour pressure, and doping concentration using positron annihilation. The Ga vacancy concentration increases with doping concentration and arsenic vapour pressure, but decreases with temperature. Using equilibrium thermodynamics, they obtained a  $-3e$  charge state of the Ga vacancy in n-doped GaAs as well as a formation enthalpy of  $(3.2 \pm 0.5)$  eV and a formation entropy of

T a b l e 1. a)

Correlation between positron trapping rate and temperature in TGS

No	Temperature °C	Positron trapping rate k [ $10^8\text{s}^{-1}$ ]
1	18	4.52
2	22	4.59
3	29	5.4
4	32	5
5	38	5.51
6	41	6.59
7	49	6
8	51	6.1
9	59	6.2
10	62	6
11	68	6.59

T a b l e 1. b)

Correlation between positron trapping rate and temperature in RS

No	Temperature °C	Positron trapping rate k [ $10^8\text{s}^{-1}$ ]
1	-40	4.9
2	-30	5.3
3	-20	5.28
4	-10	5.38
5	0	5.3
6	10	5.4
7	25	5.6
8	30	5.5
9	40	5.4
10	45	5.62

T a b l e 1. c)

Correlation between positron trapping rate and temperature in KDP

No	Temperature °C	Positron trapping rate k [ $10^8\text{s}^{-1}$ ]
1	-159	3.4
2	-153	3.2
3	-145	3
4	-140	3.6
5	-132	4
6	-120	4.4

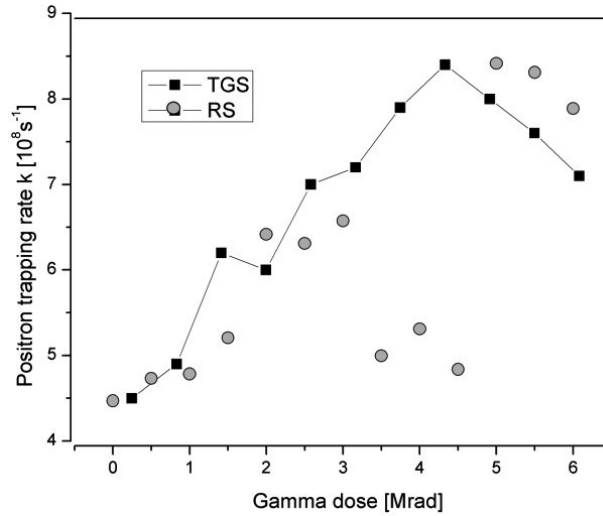


Fig. 1. Positron trapping rate as a function of gamma irradiation dose in TGS and RS

$(9.6 \pm 1) k_{\beta}$  for the uncharged vacancy state. The positron lifetime spectra were analyzed with the trapping model after source and background corrections. From the positron lifetime measurement, the trapping rate  $k_v$  of positrons into vacancies has been estimated. The positron lifetime depends mainly on the electron density at the annihilation site and provides thus information on the open volume of a defect. Further information can be obtained by studying the electron-positron annihilation momentum distribution. The studies of tellurium (Te)-doped GaAs show the competition of negatively charged vacancies and negative ions in positron trapping at low temperatures and the changes in the relative concentrations. The vacancy concentration  $c_v$  can be obtained from the positron trapping rate  $k_v$  at 550 K. They determined the trapping coefficient by quantifying the electrical compensation through  $V_{\text{Ga}}\text{-Te}_{\text{As}}$  complexes in samples having a low concentration of acceptor-type ions: i.e., where the compensation is dominated by the vacancies. Positron trapping rate into  $V_{\text{Ga}}\text{-Te}_{\text{As}}$  at 550 K as a function of the concentration of compensating acceptors. On this basis we are now able to determine the vacancy concentrations of all samples subjected to different annealing conditions. The data are from GaAs doped with Te by  $9 \times 10^{16}$ ,  $4 \times 10^{17}$ ,  $2 \times 10^{18}$  and  $6 \times 10^{18} \text{ cm}^{-3}$ , respectively. They obtain the trapping coefficient  $\mu_v = z \times (1.3 \pm 0.2) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ , where  $z$  is the charge state of the isolated Ga vacancy. Positron trapping rate in semiconductor  $V_{\text{Ga}}\text{-Te}_{\text{As}}$  at 550 K as a function of the concentration of compensating acceptors is shown in Fig. 2. The solid line is a linear fit to the data to determine the positron trapping coefficient. The data are from GaAs doped with  $9 \times 10^{16}$  (■),  $4 \times 10^{17}$  (◇),  $2 \times 10^{18}$  (●), and  $6 \times 10^{18}$  (△)  $\text{cm}^{-3}$  Te, respectively. The obtained value of trapping coefficient correlates with the charge

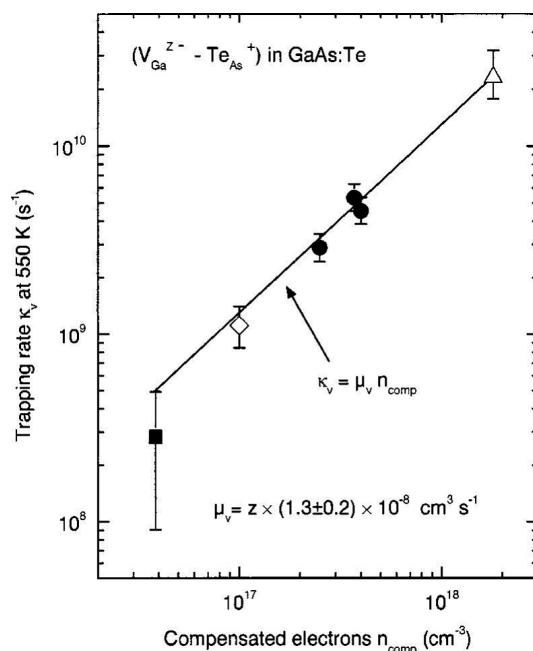


Fig. 2. Positron trapping rate into semiconductor  $V_{Ga}\text{-}Te_{As}$  at 550 K as a function of the concentration of compensating acceptors [14]

state of the isolated Ga vacancy [14]. The authors established a strong increase of the trapping rate  $k$  at 550 K with increasing of the compensated electrons.

MASCHER et al. [15] investigated dependencies between the positron trapping rates and the temperature in electron-irradiated silicon. They found that positrons annihilate with two different the trapping rates  $k_2$  and  $k_3$  as a function of isochronal annealing of the slightly n-type samples. Positron trapping rate  $k_2$  and  $k_3$  are decreasing with increase of temperature at slightly n-type semiconductor samples. Later PUSKA et al. [16] have investigated positron trapping mechanisms operative for positrons in semiconductors. Particular attention is paid to positron trapping into vacancies with various charge states. The trapping coefficient depends strongly on the height of the repulsive Coulomb barrier. For neutral vacancies the dominant trapping mechanism is found to be electron excitation from a localized state at the vacancy to the conduction band. The trapping rate coefficient is generally independent of temperature and is about  $10^{15} \text{ s}^{-1}$ . The trapping coefficients for negative vacancies are at all temperatures larger than those for neutral vacancies. The difference is enhanced at low temperatures, in which negative vacancies show  $T^{-1/2}$  divergence. It may also happen that at low temperatures, when detrapping from the Rydberg states is small, trapping into negative ions effectively competes with trapping into vacancies. KEEBLE et al. [17] demonstrated the experimental detection and identification of native

vacancy point defects in thin film and single crystal metal halide perovskite materials. Positron annihilation lifetime spectroscopy, with the aid of two-component DFT calculations, enables the identification of cation vacancy and vacancy cluster defects in MAPbI<sub>3</sub> (MA=CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>). In all the thin film and crystal samples studied a dominant,  $\geq 92\%$  intensity, positron trap with a positron state lifetime of 370(3) ps consistent with the DFT calculated value of 369 ps for V<sub>Pb</sub>. The possible trapping to (V<sub>Pb</sub>V<sub>I</sub>)<sup>-</sup> divacancy defects was observed for one of the thin film samples. The lead vacancy related defect density was found to be greater than  $\sim 3 \times 10^{15} \text{ cm}^{-3}$  in all samples. No positron trapping to MA vacancy defects was detected. The results support the predications of first-principles calculations that deep level, hole trapping, V<sub>Pb</sub><sup>2-</sup> point defects are one the most stable defects in MAPbI<sub>3</sub> and that MA vacancies are expected to have negligible concentrations. Defects created by 2-MeV electron irradiation of Czochralski-grown silicon have been investigated with use of positron-lifetime spectroscopy and results have been correlated with EPR and ir data [17]. The trapping rate for the positrons was smallest for the neutral divacancy where a concentration of  $\sim 10^{17} \text{ cm}^{-3}$  gave rise to a trapping rate of 1 ns<sup>-1</sup>. For the singly negative divacancy the trapping rate was increased at 300 K by a factor of about 3.5 and for the doubly negative divacancy a further increase by a factor of 2 was found. Isochronal annealing showed that the neutral divacancy annealed at only 150 °C, while the charged states annealed in a broad temperature range starting at 230 °C. Measurements in thermal equilibrium between 30 K and room temperature showed that shallow positron traps became activated at low temperatures. Oxygen vacancy pairs (A centres) are concluded to be the defects acting as shallow traps and yielded a lifetime of 2.5 ps, very close to the bulk lifetime of silicon. The trapping cross section of the charged defects varied with temperature as T<sup>-n</sup>, with 2 < n < 3. Since we are dealing with trapping of positively charged particles, the specific trapping rate will substantially increase when defects become negatively charged. Since the trapping rate, k<sub>3</sub>, into the neutral divacancy, V<sub>2</sub><sup>0</sup>, in the p-type sample is 0.2 ns<sup>-1</sup>, the specific trapping rate is  $2 \times 10^{-17} \text{ ns}^{-1} \text{ cm}^3$  (or  $1 \times 10^{15} \text{ s}^{-1}$  per unit divacancy concentration) [17]. KLYM et al. [18] carry out investigation of the positron trapping defects in free-volume investigation of Ge-Ga-S-CsCl glasses. The obtained spectra were deconvoluted into two positron ( $\tau_1, I_1$ ) and ( $\tau_2, I_2$ ) components and one positronium decaying ( $\tau_3, I_3$ ) component. It is found that lifetime  $\tau_2$ , intensity I<sub>2</sub> and positron trapping rate in defects k<sub>d</sub> decrease after crystallization for each of the glasses. A value of 0.311 ns<sup>-1</sup> has been established for (CsCl)<sub>0</sub> as-prepared glasses which increases to 0.762 ns<sup>-1</sup> with decrease of trapping rate to (CsCl); after that this value is constant, while for crystallized glasses the trapping rate decreases to value of 0.092 ns<sup>-1</sup> for (CsCl). This result indicates the transformation of void agglomerates with alkali halide CsCl additive into specific void contractions. Other trends are observed in (80GeS<sub>2</sub>-20Ga<sub>2</sub>S<sub>3</sub>)<sub>85</sub>(CsCl)<sub>15</sub> glasses with loose structure, where void fragmentation occurs after their crystallization.

**Conclusions.** On the based measured data of positron lifetimes in ferroelectrics, semiconductors and glasses the values positron trapping rate has been discussed. The following conclusions have been drawn: In TGS, RS and KDP at different temperature and gamma irradiation doses the existence of three positron lifetime components is established. The existence of third lifetime component is due to the positronium formation. In gamma irradiated TGS positrons are trapped in the defect states of the oxygen ions of the two radicals  $\text{CH}_2\text{COO}^-$  and  $\text{NH}_3\text{CHCOO}^-$ . The value of the positron trapping rate in gamma irradiated TGS and RS shows an increase with gamma irradiation dose. 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. Positron trapping rate in semiconductor from GaAs doped with  $9 \times 10^{16}$  (■),  $4 \times 10^{17}$  (◇),  $2 \times 10^{18}$  (●), and  $6 \times 10^{18}$  (△)  $\text{cm}^{-3}$  Te, respectively, established a strong increase of the trapping rate  $k$  at 550 K with increasing of the compensated electrons. In semiconductors, the positron trapping coefficient depends strongly on the height of the repulsive Coulomb barrier. For neutral vacancies the dominant trapping mechanism is found to be electron excitation from a localized state at the vacancy to the conduction band. The positron trapping coefficient in semiconductors is generally independent of temperature and is about  $10^{15} \text{ s}^{-1}$ . The trapping coefficients for negative vacancies are at all temperatures larger than those for neutral vacancies. These results confirm that positron annihilation techniques can characterize vacancy defects in ferroelectric materials such as TGS, RS, KDP; in semiconductor as Ga vacancies in n-type GaAs; Czochralski-grown silicon and in the Ge-Ga-S-CsCl glasses.

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