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**THE DIFFERENTIAL SCANNING CALORIMETRY AND
POSITRON ANNIHILATION LIFETIME SPECTRA STUDIES
ON AMORPHOUS AND POLYCRYSTALLINE SELENIUM
AND AMORPHOUS $\text{As}_{19}\text{Se}_{80}\text{Bi}_1$**

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The positron annihilation lifetime measurements for amorphous, retransformed and polycrystalline selenium as well as chalcogenide glass $\text{As}_{19}\text{Se}_{80}\text{Bi}_1$ before and after retransform process are presented in the paper. For controlling the thermal behavior of samples the differential scanning calorimeter (DSC) was used. It has been demonstrated that positron annihilation lifetime spectroscopy can be useful in studying the changes of physical properties during phase transitions. The best results of analysis of the positron lifetime spectra have been achieved for their decomposition into one component. The differences between amorphous and crystalline phase were manifested by distinct difference in mean positron lifetime. Because of numerous kinds of free volumes of different size application of the trapping model and deconvolution of spectra into many components contributing to individual free volumes for investigated materials was impossible.

Key words: positron annihilation, amorphous semiconductors, glasses, chalcogenides, deconvolution, lifetime components.

Positron annihilation lifetime spectroscopy (PALS) is a relatively novel technique based on investigations of annihilation behavior of positron or positronium, i.e. a bound system of positron and electron. Positrons are very sensitive indicators of the local electron density distribution in condensed matter [1]. PALS is also standard technique in detection of crystalline defects such as vacancies, dislocations (e.g. [2]) and free volumes in the amorphous phase, especially in polymers (e.g. [3]). The dimensions of free volumes and local electron density affect the mean lifetime of annihilating positrons. It is possible that positron annihilation parameters reflect two or three dominating types of free volumes by differentiating independent channels of annihilation. For analysis of positron annihilation lifetime spectra, standard computer program can be used, eg. LT [4]. The deconvolution of a spectrum includes background and source contribution extraction and decomposition of the remaining part of spectrum into lifetime components. When there are favorable conditions of positronium formation, which is limited by dimensions of free volumes, the lifetime components can be ascribed to dominating types using standard quantum-mechanical model of ortho-positronium in spherical hole [3]. The presence of positronium in a sample is manifested

by lifetime component of the order of nanoseconds related to ortho-positronium. Another component with corresponding lifetime of 0,125 ns is characteristic for para-positronium. The intermediate component having mean lifetime of 0,2–0,4 ns characteristic for all amorphous materials is also present in a spectrum. This component reflects annihilation of free positrons in condensed matrices.

When dimensional conditions for positronium formation are not fulfilled and there is no any dominating type, or too many types of free volumes are present in an amorphous sample, the PALS can not inform about dimensions of holes, but positrons can be used to examine local changes of electron density and hence to detect changes occurring during phase transitions or other subtle effects by non-destructive way. In that case the decomposition of spectra into more than one component is faced with difficulties of interpretation. The deconvolution of the spectra into more than one component could mean, e.g. that for many different free volumes in amorphous matrices some of volumes are preferred by positrons. In the paper we try such possibility for two different materials.

The abilities of PALS in aspect of detecting the phase transitions between amorphous and crystalline state as well as between amorphous and retransformed state (the product of retransforming process is relaxed glassy material with structure characteristic for supercooled liquid phase) are examined.

For our investigations metallic selenium and chalcogenide glass ($\text{As}_{19}\text{Se}_{80}\text{Bi}_1$) have been chosen. The amorphous phase of selenium can be prepared by an easy process of quenching of liquid selenium in water at room temperature. Heating the sample at only 345 K during first run and at 415 K during second run enabled preparation of retransformed and crystalline phase of material, respectively. Another investigated sample, $\text{As}_{19}\text{Se}_{80}\text{Bi}_1$ was also amorphous before thermal treating. The annealing of the sample at 395 K generated endothermic process. This small thermal effect is not necessary connected with detectable changes of local electron densities by positron annihilation methods. We were going to check the ability of PALS in such application.

For controlling the thermal behavior of samples the differential scanning calorimeter (DSC) was used.

It is worth to say that chalcogenide glasses are prospective disordered materials for applications in optoelectronics, photonics, telecommunications, acousto-optics, etc. [5]. The amorphous selenium belongs to the group of semiconductors which are also subject of intensive research effort spurred by both the scientific and technological interest. It is considered as prospective material in numerous advanced technological applications (microelectronics, optoelectronics etc.) [6].

The samples of selenium were prepared from metallic, 99,999 % of purity material, supplied by POCh Gliwice. The amorphous phase was produced by quenching a stream of liquid selenium, tempered at 570 K, in water at room temperature. Annealing of samples in air during 30 min at 345 K enabled first phase transition (retransforming). Another 30 min of annealing at 415 K have effected in second phase transition of the samples.

The amorphous $\text{As}_{19}\text{Se}_{80}\text{Bi}_1$ samples were prepared by conventional melting of appropriate mixture of high purity (99,999 %) precursors in evacuated quartz ampoules, followed by air quenching to room temperature. The samples were annealed at 395 K during 30 min to pass through an endothermic effect.

Positron Annihilation Lifetime spectra were obtained using the conventional fast-slow coincidence spectrometer with BaF_2 scintillators coupled to Philips XP2020Q

photomultipliers. The time resolution of the device was determined as the value of full weight at half maximum (FWHM) of resolution curve given by lifetime computer program (LT) [4] for each of the spectrum. The mean value of FWHM determined from 5 spectra equals to 274 ps. The 90° geometry of detectors was applied. A $20 \mu\text{Ci } ^{22}\text{Na}$ positron source sealed by hostaphan foils was placed between two plates of the same samples. The mean value of counts for a spectrum exceeds $1,3 \cdot 10^6$. The spectra were deconvoluted into one component. The results of deconvolution of spectra into two or more (not fixed) components are presented in the paper, too. All the positron annihilation lifetime measurements were performed in air, at room temperature.

The calorimetric measurements of the samples were performed using the Netzsch DSC 404/3F differential calorimeter with E-type measuring head and high-density Al_2O_3 sample pans. All the differential thermal analyses (DTA) were performed in air.

The DTA curve for as quenched selenium sample registered at the heating rate of 20 K/min in the temperature range extending from room temperature to 550 K, is presented in Fig. 1.

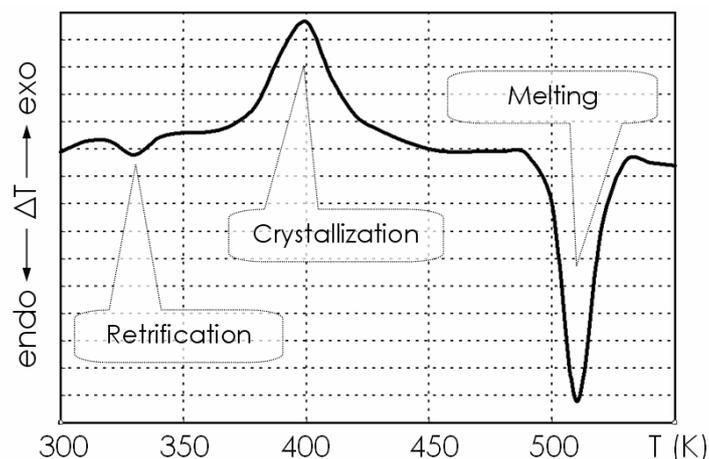


Fig. 1. DTA thermogram of as quenched amorphous selenium sample registered at a heating rate of 20 K/min

Three thermal effects are clearly visible on this thermogram: a weak low-temperature endotherm (320–330 K) connected with the retrification process, the product of which is the relaxed glassy selenium with structure corresponding to that of overcooled liquid phase and distinct exotherm (370–430 K) corresponding to crystallization of glassy selenium. With further rising of the temperature, the crystalline selenium melts, which is manifested by an intensive endotherm (490–520 K).

The results of analysis of positron lifetime spectra by LT program for amorphous, retrificated and crystalline selenium are presented in the table 1.

Table 1

Results of the analysis of experimentally determined positron lifetime spectra for amorphous, retransformed and crystallized selenium

Investigated material	Deconvolution into one component		Deconvolution into two components			
	τ_1 (ps)	Fit's variance	τ_1 (ps)	I_1 (%)	τ_2 (ps)	Fit's variance
Amorphous Selenium	302,8 (1,2)*	1,0355	21 (10)	8,5 (1,6)	291,9 (1,0)	0,9886
Retrified Selenium	303,1 (1,0)	1,0700	0,0 (13)	3,13 (0,19)	303,5 (1,0)	1,0781
Crystallized Selenium	291,0 (1,0)	1,0043	303 (16)	66,9 (74,1)	303 (90)	1,0370

* – Standard deviations are given in round brackets.

In the analysis of the positron lifetime spectra of amorphous, retransformed and crystalline selenium, a long-lifetime component of the nanosecond order of magnitude was looked for. Such component is generally assigned to ortho-positronium formation and decay in disordered regions of condensed materials. There is lack of nanosecond component in the spectra for not fixed values of lifetime, independent of one or two component deconvolution. Fixing of nanosecond component generates the values of intensities on the level comparable to the background.

The deconvolution of the spectra into two, not fixed components generally failed either. For the retransformed selenium the value of mean lifetime corresponding to the first component equals to zero. It would mean that all the positrons contributed to that component annihilated immediately after thermalization. It is certainly impossible. For the crystalline selenium the LT program generated two independent components with the same values of τ_1 (303 ps). For the amorphous selenium the first component with τ_1 of 21 ps is hardly interpreted taking into account that for all the elements, the bulk lifetimes are never less than 96 ps [7]. Additionally, standard deviations of lifetimes and intensities for two component analysis are considerably greater than that for one component, so only the data described by one component are reliable.

In polycrystalline sample, point defects in the concentration corresponding to the thermodynamical equilibrium as well as grain boundaries known as disordered regions are present. It may be a bit wondering, that analysis of the data did not reveal the defect component. We think, that even if positrons annihilate from such trapped states the insignificant number of such acts does not influences positron annihilation parameters.

In amorphous samples positrons can annihilate within many different types of free volumes. The deconvolution of spectra for such materials into more than one components corresponding to different free volumes is limited by uncertainties of the used method of analysis. From practical point of view when positronium can be formed, a deconvolution of a spectrum into not more than four lifetime components is reliable, for amorphous materials, for which positronium can not be formed – two components could be controversial. We believe that deconvolution of spectra into one component and having information on a mean lifetime of positrons in such situation is the best information one can have.

The mean lifetime for amorphous selenium equals to 302,8 ps, and is greater than that for crystalline selenium – 291,0 ps. If the probability of trapping of positrons in both the materials is the same, the difference in measured lifetime reflects the differences in local electron density. The mass density for amorphous selenium, $4280 \pm 40 \text{ kg/m}^3$ is smaller than that for crystalline material – 4820 kg/m^3 [12] and hence the local electron density of crystalline material is greater than that for amorphous one. It explains the differences in lifetimes between amorphous and crystalline material.

The PALS did not reveal the differences between mean lifetime for amorphous and retransformed selenium. This result is not astonishing. We expected much less differences for that pair of samples in comparison with amorphous and crystalline materials, where structural differences connected with changes of mass density and local electron density are considerably greater.

During thermal investigations of chalcogenide glass of $\text{As}_{19}\text{Se}_{80}\text{Bi}_1$ the sample was twice heated with 5 K/min from room temperature to 425 K. The results of measurements are presented on Fig. 2.

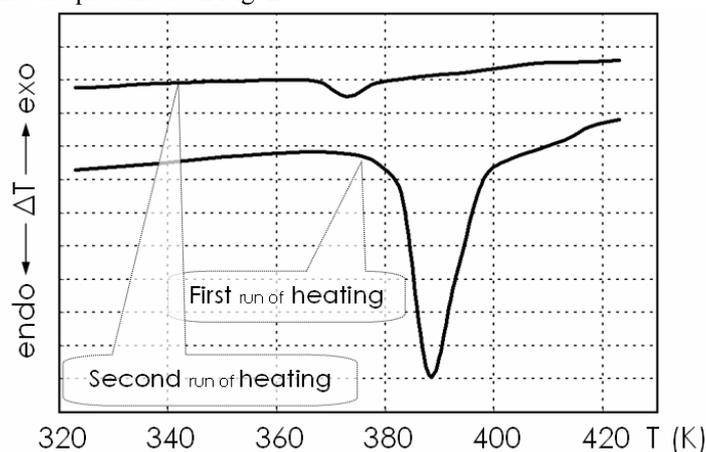


Fig. 2. DTA thermogram for the samples of chalcogenide glass $\text{As}_{19}\text{Se}_{80}\text{Bi}_1$ registered at a heating rate of 5 K/min for first and second heating run

There are clearly visible endothermic peaks for each cycle of heating on the thermogram. For the first run the number of energy absorbed by sample is much greater than for second. If the effect is connected with relaxing mechanisms then it is seen that the process of relaxation after first run is not complete. The positron annihilation lifetime spectra were measured before and after first run of heating. The results of lifetime measurements are presented in table 2.

Similarly to the selenium material a small effect for chalcogenide glass of $\text{As}_{19}\text{Se}_{80}\text{Bi}_1$ was expected. However, it is surprising that mean lifetime for the retransformed sample is greater than that for amorphous sample. The difference is 4,4 ps and is not much more than standard deviation estimated on 2 ps. It can mean that the process of relaxation of $\text{As}_{19}\text{Se}_{80}\text{Bi}_1$ is not complete and the final result could be achieved after a few cycles of heating. The DTA measurements confirm that. The attempt of deconvolution of spectra for the $\text{As}_{19}\text{Se}_{80}\text{Bi}_1$ sample into two components failed. The similar behavior was observed for the selenium. The received lifetimes

corresponding to the first component are definitely too small and corresponding standard deviations are too high. Therefore, the results of two component deconvolution are not reliable. There is lack of positronium component having lifetime of the order of ns.

Table 2

Results of the analysis of experimentally determined positron lifetime spectra for chalcogenide glass $As_{19}Se_{80}Bi_1$

Investigated material	Deconvolution into one component		Deconvolution into two components			
	τ_1 (ps)	Fit's variance	τ_1 (ps)	I_1 (%)	τ_2 (ps)	Fit's variance
Amorphous $As_{19}Se_{80}Bi_1$	305,1 (1,0)	1,0550	36 (16)	4,9 (1,5)	306,2 (1,0)	0,9524
Retrified $As_{19}Se_{80}Bi_1$	309,5 (1,0)	0,9627	28 (12)	6,4 (2,4)	310,6 (1,0)	1,0466

*- Standard deviations are given in round brackets.

The results of measurements demonstrate that positronium do not exist in both investigated amorphous materials, (Se, $As_{19}Se_{80}Bi_1$). The best results of analysis of the spectra have been achieved for their decomposition into one component. For investigated materials the differences between amorphous and crystalline phase is manifested by distinct difference in mean positron lifetime. Taking into account that annihilation process is not destructive for samples, the PALS can be used as efficient tool for monitoring structural transitions connected with changes of local density of electrons. Because of numerous kinds of free volumes of different size using of trapping model and deconvolution of spectra into many components contributing to individual free volumes was impossible.

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**ВИВЧЕННЯ ПОЛІКРИСТАЛІЧНОГО СЕЛЕНУ ТА АМОРФНОГО
As₁₉Se₈₀Bi₁ МЕТОДАМИ ДИФЕРЕНЦІЙНО-СКАНУВАЛЬНОЇ
КАЛОРИМЕТРІЇ ТА ПОЗИТРОННОЇ АНІГІЛЯЦІЙНОЇ СПЕКТРОСКОПІЇ**

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В роботі представлено результати досліджень полікристалічного селену та халькогенідного скла As₁₉Se₈₀Bi₁ методом позитронної анігіляційної спектроскопії. Для контролю термічної залежності зразків використано диференційно скануючу калориметрію. Показано, що метод позитронної анігіляції може успішно використовуватись для вивчення фізичних властивостей під час фазових переходів. Найкращі результати були отримані під час розкладу спектра на одну компоненту. Відмінності між аморфною та кристалічною фазами проявляється в різниці середнього часу життя позитронів.

Ключові слова: позитронна анігіляційна спектроскопія, аморфні напівпровідники, халькогенідні стекла, деконволюція, час життя компонент.

**ИЗУЧЕНИЕ ПОЛІКРИСТАЛЛИЧЕСКОГО СЕЛЕНА И АМОРФНОГО
As₁₉Se₈₀Bi₁ МЕТОДАМИ ДИФФЕРЕНЦИАЛЬНО-СКАНИРУЮЩЕЙ
КАЛОРИМЕТРИИ И ПОЗИТРОННОЙ АНИГИЛЯЦИОННОЙ
СПЕКТРОСКОПИИ**

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В работе представлены результаты исследований поликристаллического селена и халькогенидного стекла As₁₉Se₈₀Bi₁ методом позитронной анигиляционной спектроскопии. Для контроля термической зависимости образцов использовано дифференциально-сканирующую калориметрию. Показано, что метод позитронной анигиляции может успешно использоваться для изучения физических свойств во время фазовых переходов. Наилучшие результаты было получено при разложении спектра на одну компоненту. Отличия между аморфной и кристаллической фазой проявляются в разнице среднего времени жизни позитронов.

Ключевые слова: позитронная анигиляционная спектроскопия, аморфные полупроводники, халькогенидные стекла, деконволюция, время жизни компонент.

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