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METHODOLOGICAL APPROACH AND TREATMENT ALGORITHMS FOR PAL DATA OF NANOMATERIALS USING COMPUTER-BASED SYSTEMS

The new modified specialized computer-based systems for experimental study of defect-related and adsorption-desorption processes in nanostructured ceramics and glasses with using of positron annihilation lifetime spectroscopy was developed. The mathematical approach to the treatment of positron annihilation lifetime data in humidity-sensitive ceramics as well as algorithm of the positron annihilation lifetime data processing in semiconducting glasses was proposed. It is shown that water-sorption processes in ceramics leads to increase in positron trapping rates of extended defects located near grain boundaries. The fixation of direct positron lifetime components allows refining the most significant changes in positron trapping rate of defects.

Key words: *annihilation measurements systems, positron annihilation, spectroscopy, water-sorption processes, structural analysis.*

Introduction

Positron annihilation lifetime (PAL) spectroscopy provides a high potential for characterization of local free volumes in the material on a subnanometer scale [1,2]. It is frequently used for studying of spatial heterogeneities in crystals, liquids and polymers, but less commonly for ceramics and semiconducting glassy alloy [3]. Recently, it was shown that the amount of adsorbed water in such perspective materials for humidity sensors as nanostructured spinel $MgAl_2O_4$ ceramics with uniform porous structure affects not only their electrical conductivity, but also positron trapping modes of extended defects tested with PAL spectroscopy [4-6]. In the case of semiconducting glasses, correct algorithm of PAL data should be developed with include an error analysis associated with geometry of PAL measurements, appropriate statistics of the events and proper background removal.

In this paper, new modified specialized computer systems for experimental study of defect-related and adsorption-desorption processes in nanostructured ceramics and glasses with using of PAL spectroscopy should be developed. In addition, to refine the most significant changes in positron trapping in $MgAl_2O_4$ ceramics caused by water sorption.

1. Technical aspects of the PAL systems

Traditional, the PAL measurements were performed with an ORTEC spectrometer [1] with [22]Na source placed between two ceramic samples (Fig. 1).

The PAL spectra were recorded with fast coincidence system of 230 ps resolution at the temperature T = 22 °C and relative humidity RH = 35 %, provided by special climatic installation. Two identical aged or rejuvenated samples were used to build a sandwich structure needed for PAL measurements. The obtained results agreed well with each other within an experimental error-bar. Each spectrum was measured with a channel width of 6.15 ps and contained ~10^6 coincidences in total, which can be considered as normal measurement statistics.

For study of nanostructured humidity-sensitive materials at different relative humidity RH (for example, in cycles 25-60-98-60-25 %) the chamber (Fig. 2) with specialized humidity control PID+ was design (Fig. 3).
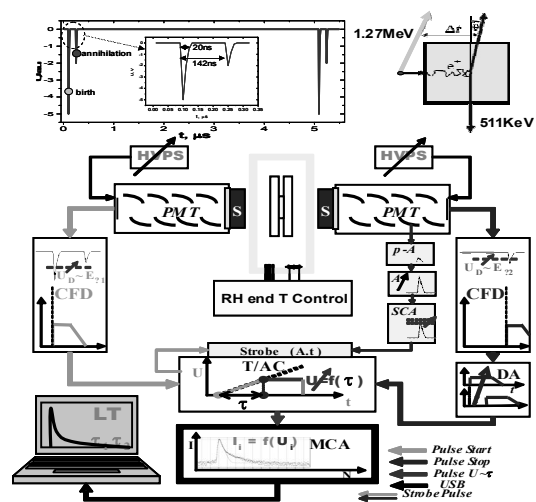

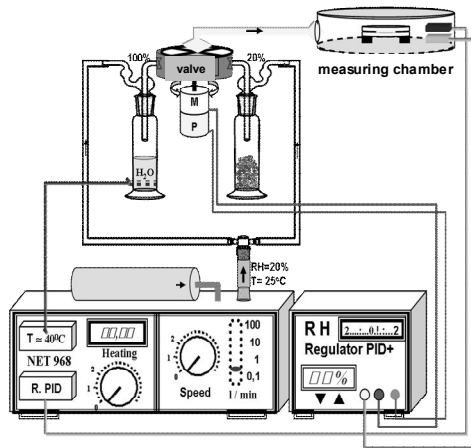Fig. 1. Experimental setup for measurement of PAL spectra with ORTEC spectrometer [1]

Fig. 2. Measuring humidity chamber. Thermal stability parameters for studied samples during long-term measurements provided by the system controllers
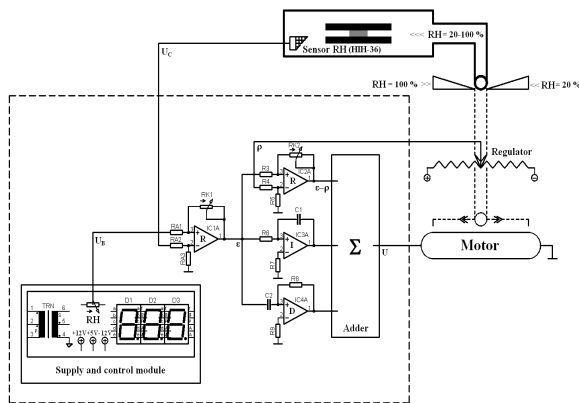

Fig. 3. Schematic of humidity control instrument PID+

In Fig. 3: U_B – turn-on voltage; U_c – output voltage of humidity sensor; $\varepsilon(t)$ – difference between the set and necessary values: $\varepsilon \sim U_B - U_c$; $\rho(t)$ – regulator voltage; R – difference input in amplification regulation: k_1 (RK1), k_2 (RK2); I – integration input in the general time regulation T_i (R6, C1), D –difference input in detection loss regulation T_d (R8, C2), Σ –adder input from input voltage controlling by voltage amplifier:

$$u(t) = k_1 \left[\left(\varepsilon(t) - \rho(t)\frac{k_2}{k_1} \right) + \frac{1}{T_i} \int_0^{T_i} \varepsilon(t)dt + T_d \frac{de(t)}{dt} \right], (1)$$

where k_1=RK1/RA1, k_2=RK2/R3, T_i=C1·R6 and T_d=C2·R8. These values for measuring chamber were experimental selected based on previous calculations in accordance with Zieglera-Nicholsa criteria.

The selection of corresponding values for measuring chamber permit to investigation of samples at constant values of RH in the range of 25-60 % with an accuracy of ± 0.5 % and 60-98 % з with an accuracy of ± 1 %. The obtained data were mathematically treated with LT 9.0 computer program of J. Kansy [5] at three-component fitting procedure with the fixed positron lifetimes τ_1 and τ_2. The proposed algorithm of treatment

of PALS data for humidity-sensitive nanomaterials was shown in Fig. 4. Using formalism for two-state positron trapping model [1], the following parameters can be calculated [3, 5]:

$$\kappa_d = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_2} \right), \quad \tau_b = \frac{I_1 + I_2}{\dfrac{I_1}{\tau_1} + \dfrac{I_2}{\tau_2}} \quad \tau_{av} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}$$

where κ_d is positron trapping rate in defect, τ_b – positron lifetime in defect-free bulk and $\tau_{av.}$ – average positron lifetime. The difference ($\tau_2 - \tau_b$) can be accepted as a size measure of extended defects, as well as the τ_2/τ_b ratio represents the nature of these defects [3].
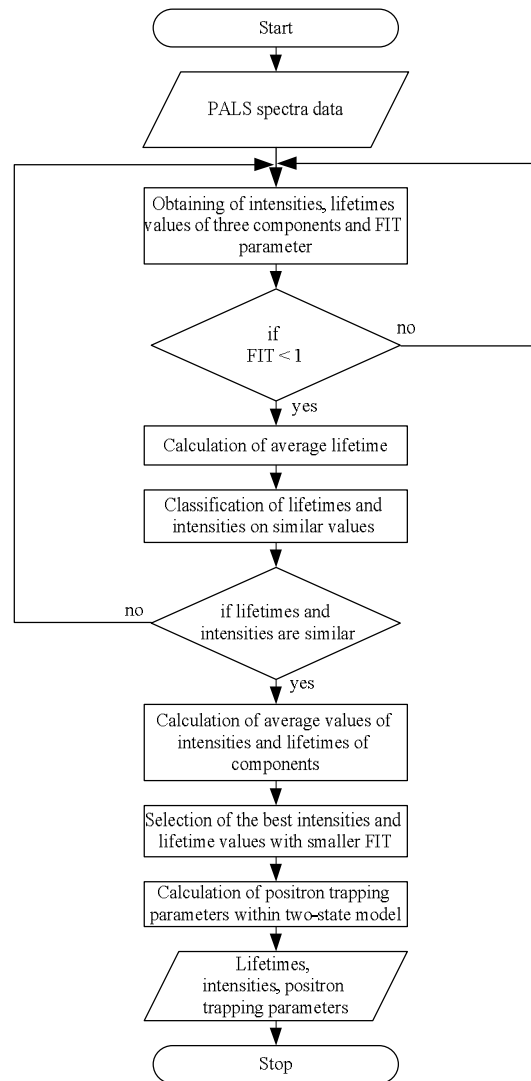

Fig. 4. Algorithm of treatment of PAL data [7]

2. Modified digital PAL spectrometer

To accelerate the process of measuring of PAL spectra, the modification of spectrometer can be used (Fig. 5). Such modification allows measurements for 4 s, while at using of traditional spectrometer ORTEC this value is 3 hours. Scintillation pulse is stored in memory

as a sequence of 10-bit numbers. Use trigger will get time registration near 4 ÷ 20 s. Select the memory area, which depends on the participation of long-term component in the spectrum, does not affect the resolution of the process.

Technical solutions proposed method synchronization and startup can be arbitrary, depending on the parameters used card processing and archiving of A\D. Advantages over the traditional and modified spectrometer was shown in Table 1.
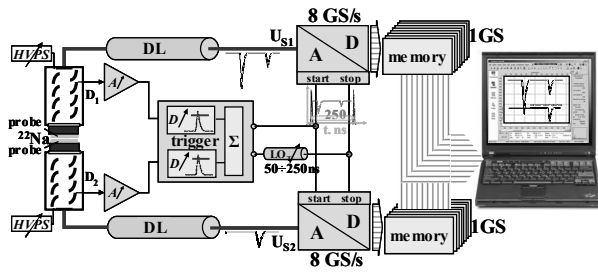

Fig. 5 Modified digital PAL spectrometer

Table 1.
Parameters of traditional and modified spectrometer

Parameters	ORTEC	Modified
Treatment rate, c^{-1}	~100	~250
Base time, c	200	250
Duration of treatment	~3 h	~ 4 s

3. Experimental results for nanostructured ceramics

The studied $MgAl_2O_4$ ceramics were sintered from fine-dispersive Al_2O_3 and MgO powders using a special regime with maximal temperatures of 1200 and 1300 °C, the total duration being 2 h [8].

The previous PAL measurements in the studied ceramics sintered at 1200 °C was performed at 20 °C and 35 % relative humidity without special testing procedure without standard thermally-treated non-defected Ni and Al probes. The best results were obtained at three-component fitting procedure with corresponding positron lifetimes and intensities ($\tau_1 = 0.18$ ns, $I_1 = 74$ %; $\tau_2 = 0.38$ ns, $I_2 = 25$ % and $\tau_3 = 1.88$ ns, $I_3 = 2$ %). Since the water sorption reveals catalytic effect on positron trapping modes in $MgAl_2O_4$ ceramics, in our investigations, we decided to fix all water-dependent positron trapping inputs in $MgAl_2O_4$ ceramics with the different contest of adsorbed water.

This approach can be well realized by fixing short positron lifetime τ_1, which reflects microstructure specificity of spinel ceramics, as well as middle defect-related positron lifetime τ_2, which corresponds to extended defects located near intergranual boundaries, where the studied ceramics are more defective. It was

shown in [8], the positrons are trapped in the same extended defects located near intergranual boundaries both in as-prepared and water-moistened ceramic samples. In accordance with these data, the lifetime τ_2 can be also fixed. At such methodological approach, changes in the fitting parameters of the first and second lifetime components of PAL spectra connecting with the different amount of adsorbed water in ceramics will be reflected in intensities I_1 and I_2. Within this approach and taking into account the previous data obtained for $MgAl_2O_4$ ceramics sintered at 1200 and 1300 °C, the lifetimes τ_1 and τ_2 were fixed at the levels of 0.18 and 0.38 ns, respectively for ceramics sintered at 1200 °C and fixed at the levels of 0.17 and 0.36 ns, respectively for ceramics sintered at 1300 °C. In addition, with the aim of obtaining of minimal FIT, the lifetimes of these two components were also fixed on a typical for $MgAl_2O_4$ ceramics values, such as 0.17-0.19 ns (for τ_1 lifetime) and 0.30-0.33-0.36-0.38 ns (for τ_2 lifetime). Nevertheless, the best FIT was obtained at fixed lifetimes $\tau_1 = 0.17$-0.18 ns and $\tau_2 = 0.36$-0.38 ns.

As it is shown on Fig. 6, the intensities of the second component I_2 increase at water adsorption from 25 to 98 % and decrease from 98 to 25 %.
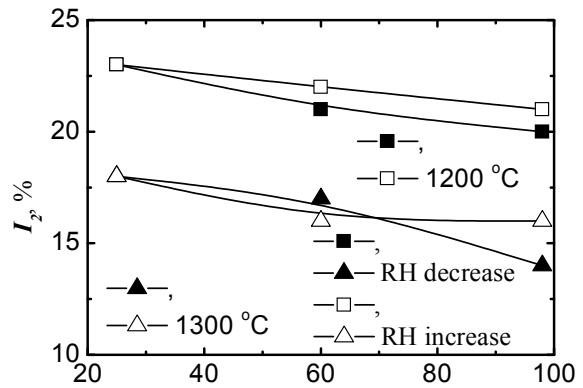

Fig. 6. Dependence of intensity I_2 from relative humidity RH for ceramics sintered at 1200 and 1300 °C

Thus, the positron trapping in water-filled defects occurs more intensive. The intensity I_1 of the first component decrease at water adsorption by ceramic nanopores with relative humidity and increase at water desorption with RH = 98-25 %. The lifetime τ_3 decrease from 2.37 to 2.27 ns with decrease of RH from 98 to 25 % but I_3 intensity leaves at the same level 1 %. Thus, this channel is non-significant during process of water sorption. Only at the so-called "forced" filling of all volume of nanopores, this channel feels physically water-sorption that shows up in the increase of I_3.

The positron trapping rate in defect κ_d considerable increases from 0.59 ns^{-1} at 98 % RH to 0.67 ns^{-1} at 25 % RH and decrease from 0.67 ns^{-1} at 25 % RH to 0.61 ns^{-1} at 98 % RH (Fig. 7) and increase from 0.45 ns^{-}

^{1} at 98 % RH to 0.57 ns^{-1} at 25 % RH and decrease from 0.57 ns^{-1} at 25 % RH to 0.50 ns^{-1} at 98 %.
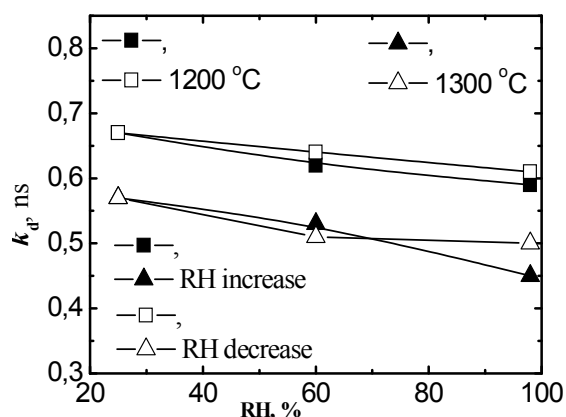

Fig. 7. Dependence of positron trapping rate in defect κ_d from RH for ceramics sintered at 1200 and 1300 ^{o}C

3. Algorithm of PAL data in glass

Usually, to provide nondestructive conditions of PAL measurements, the positron source wrapped with Kapton$^{®}$ is sandwiched between the two identical ChG samples as it is shown in Fig. 8.

If high-power positron sources are used (to provide high statistics of measurements), the amount of radioactive salt which should be wrapped with Kapton$^{®}$ is significant, that leads to non-flat surfaces of positron source placed between the samples. As a result, some positrons annihilate not in the samples bulk, but in the area between the samples in the sandwich structure. The long-lived component appears in the PAL spectrum of ChG in comparison to the measurements performed in perfectly aligned sandwich structure (Fig. 8). Then, if such distorted spectrum is analyzed, the obtained parameters of positron annihilation do not reflect only the open-volume defects in ChG, but also the effects inside sandwich structure. Therefore, a lot of attention should be paid on the preparation procedure of sandwich setup. In particular, there should be no space between the samples and positron source. Another source of inaccuracies can be introduced by incorrect accounting of source contribution into PAL spectrum, because Kapton$^{®}$, which wrap the positron source, has average lifetime (~372 ps) comparable with second lifetime component of positrons in ChG.

Next step is the analysis of PAL spectra itself. Typical spectrum obtained by PAL technique usually includes the noisy decaying part towards larger positron lifetimes. We have performed the analysis of PAL spectrum by LT 9.0 software including different number of channels starting from the whole spectrum (2200 channels) and restricting it gradually to the less noisy data (down to 1500 channels).
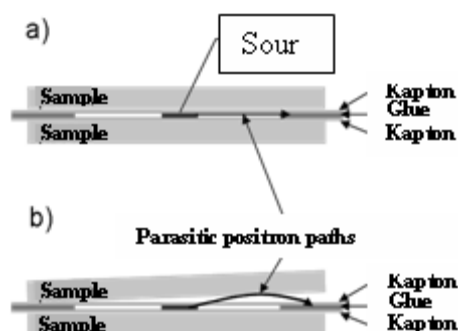

Fig. 8. Sample's setup for PAL measurements [9]

It can be easily seen, that background significantly influences the PAL parameters as obtained with LT program. Including more background noisy data into the analysis (more channels are analyzed) significantly increases average positron lifetime values and τ_b as obtained from the analysis [9,10]. This can explain discrepancy of PAL parameters obtained by different authors for same glasses. Indeed, if obtained PAL spectra are decomposed into two components, the parameters of fitting components change drastically. At the same time, the quality of fitting exhibits a minimum for a number of included channels between 1550 and 1750. This minimum corresponds to the most reliable data analysis of the raw PAL spectra.

Conclusions

The new modified specialized computer systems for experimental study of defect-related and adsorption-desorption processes in nanostructured ceramics and glasses with using of PAL spectroscopy was developed. The mathematical treatment of PAL data allows to refine the most significant changes caused by absorbed water in the spinel ceramics. Correct algorithm of PAL data analysis for glasses should include an error analysis associated with geometry of PAL measurements, appropriate statistics of the annihilation events and proper background removal.

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МЕТОДОЛОГІЧНИЙ ПІДХІД ТА АЛГОРИТМИ ОПРАЦЮВАННЯ ПАС ДАНИХ НАНОМАТЕРІАЛІВ З ВИКОРИСТАННЯМ КОМП'ЮТЕРНОЇ СИСТЕМИ

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В роботі запропоновано модифіковану комп'ютеризовану систему для експериментального дослідження адсорбційно-десорбційних та дефектних процесів в наноструктурованій кераміці та склі з використанням позитронної анігіляційної спектроскопії (ПАС). Запропоновано математичний підхід до опрацювання даних ПАС для волого-чутливої нанокераміки, а також алгоритм обробки даних для напівпровідникових стеклах. Показано, що волого-сорбційні процеси в кераміці призводять до збільшення швидкості захоплення позитронів дефектами, які зосереджені на границях зерен. Фіксація часів життя дефектної компоненти дозволяє відобразити зміни у швидкості захоплення позитронів дефектами.

Ключові слова: система анігіляційних вимірювань, позитронна анігіляція, спектроскопія, волого-сорбційні процеси, структурний аналіз.

МЕТОДОЛОГИЧЕСКИЙ ПОДХОД И АЛГОРИТМЫ ОБРАБОТКИ ПАС ДАННЫХ НАНОМАТЕРИАЛОВ С ИСПОЛЬЗОВАНИЕМ КОМПЬЮТЕРНОЙ СИСТЕМЫ

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В работе предложено модифицированную компьютеризированную систему для экспериментального исследования адсорбционно-десорбционных и дефектных процессов в керамике и стекле с использованием позитронной аннигиляционный спектроскопии (ПАС). Предложено математический подход к обработке данных ПАС для влагочувствительной нанокерамики, а также алгоритм обработки данных для полупроводниковых стекол. Показано, что влагосорбционные процессы в керамике приводят к увеличению скорости захвата позитронов дефектами, которые сосредоточены на границах зерен. Фиксация времен жизни дефектной компоненты позволяет отразить изменения в скорости захвата позитронов дефектами.

Ключевые слова: система аннигиляционных измерений, позитронная аннигиляция, спектроскопия, влагосорбционные процессы, структурный анализ.

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