Confined water in controlled pore glass CPG-10-120 studied by positron annihilation lifetime spectroscopy and differential scanning calorimetry

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Abstract. The solidification and melting of water confined in the controlled pore glass (CPG) with average pore size 12.6 nm has been studied by differential scanning calorimetry (DSC) and positron annihilation lifetime spectroscopy (PALS). The fully-filled sample of CPG by water as well as the samples of CPG with different content of water were used. The measurements show the presence of amorphous and crystalline phases of water in this type and size of pores, freezing point depression of a confined liquid and presence of certain transitions at lower temperatures, which could be detected only for cooling regime. The localization of confined water in the partially filled pores of CPG at room temperature was studied.

1. Introduction

Porous materials with nanometer size pores are extensively exploited in science and technology. They are used as adsorbents, catalyst support and chromatographic packings. Such materials can suppress the crystallization of confined materials and allow to prepare different structures in comparison with bulk state [1]. Water belongs to the most important substances in nature and is essential for the life. The knowledge of water properties in confined systems is very important, because water exhibits complicated behaviour and many anomalies [2,3].

Systematic research of confined systems associating differential scanning calorimetry (DSC) and positron annihilation lifetime spectroscopy (PALS) methods has been launched [4-6]. The localization of confined liquid in the pores of the matrix in the case of partially-filled pores is also interesting information [6]. In the present study, the thermal behaviour of water solidified in the controlled pore glass CPG-10-120 of mesoporous category (12.6 nm average pore size) as well as the localization of water in the partially-filled pores at room temperature are investigated. The results are compared with the study of the bulk water and ice by positron annihilation method [7].

2. Experimental

For this study CPG-10-120 obtained from BDH Chemicals Ltd., England with mean pore diameter 12.6 nm, pore volume 0.87 mL g^{-1} and pore surface area 187.1 m^2 g^{-1} has been used. This mesoporous material prepared by specific thermal treatment of borosilicate glass [5] with narrow size pore distribution (± 7.8 %, information from producer) is characterised by sponge-like morphology. The

distilled water (standard laboratory quality) was used. The process of water filling was based on the action of capillary forces, which pulled defined quantity of water into the pores (filled in air). The partial mass of water (or coefficient of filling) in each sample is defined as $k = m_{H2O}/(m_{H2O} + m_{CPG})$, where m_{H2O} and m_{CPG} is mass of water and CPG ($\pm$ 0.1 %), respectively, in the prepared sample.

The DSC measurements were performed using power-compensation DSC8500 (Perkin-Elmer) with automatic intracooler (200 K). Samples of 15 – 30 mg encapsulated in air and measured in dynamic nitrogen atmosphere were used. Continuous cooling and heating regimes with the rates of 2 K min^{-1} were applied. The precision of the measured data is $\pm$ 0.4 K and $\pm$ 2 J g^{-1}.
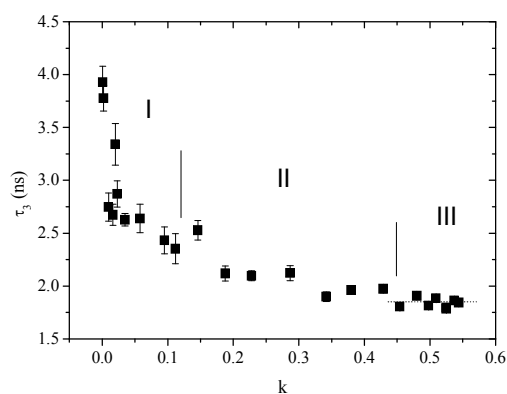
The low-temperature dependence of o-Ps lifetimes in the CPG/water composite for the $k = 0.522$ in the temperature region 60-300 K (closed cycle He-refrigerator, temperature stability better then 1K) was studied by PALS. At room temperature the samples with different content of water (sequential evaporation of water from the primary sample with $k = 0.522$) were investigated also. Lifetime spectra were measured by the conventional fast-fast coincidence time spectrometer with the time resolution about 320 ps FWHM determined by Al defect-free sample. PATFIT-88/POSITRONFIT [8] code was used for the analysis. The correction on the positron annihilation in the source as well as in the sample container Kapton foil window was taken into account. The free volume pore sizes were estimated from the o-Ps lifetime using EELViS routine [9] for the spherical cavity.

3. Results and discussion

PALS results for o-Ps lifetimes and their relative intensities for the different k at room temperature in air are in Figs. 1-3 (four-component analysis used). The τ_4 (k) dependence shows uniform value and I_4 increases with decreasing of k in large range of k (0.12-0.45, area II on figures). Water gradually escapes from large pores without creating of thick layer on the CPG inner pore surface. In fully-filled and over-filled samples I_4 is negligible (τ_4 with large errors, $k>0.45$, area III) and τ_3 is similar to the value of liquid bulk water. For low content of water ($k<0.12$, area I) τ_3 increases more evident with decreasing k. This effect is connected with an influence of similar value of o-Ps lifetime in small pores in pure matrix ($k=0$) and creation of additional small free-volumes, when monolayer of water on pore surface is probably crushing whenever water escapes from pore surfaces.
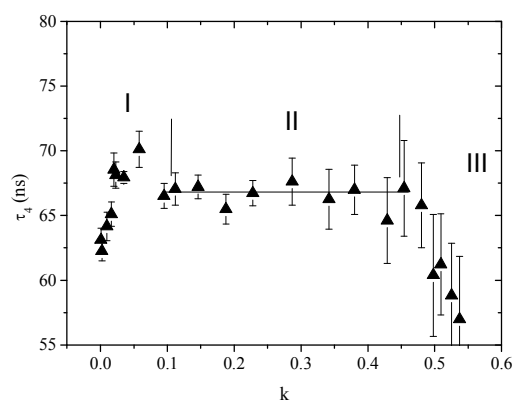

Figure 1. Dependence of o-Ps lifetime τ_4 (connected with large CPG pores) on the coefficient of filling k.

Figure 2. Dependence of o-Ps lifetime τ_3 on the coefficient of filling k.

The temperature dependence of o-Ps lifetime τ_3 (Fig. 5, three-component fit was used) for the region 260-300 K is very similar to that of bulk water. The sharp change of the τ_3 at phase transition of water to ice presented at the bulk state [7] is absent in confined system. The global trends in the

temperature dependence change here gradually, indicating a less ordered structure and being similar to amorphous systems. Thence τ_3 is so high at low temperature compared with bulk water value.
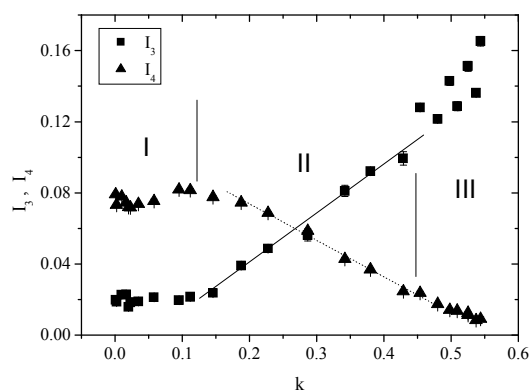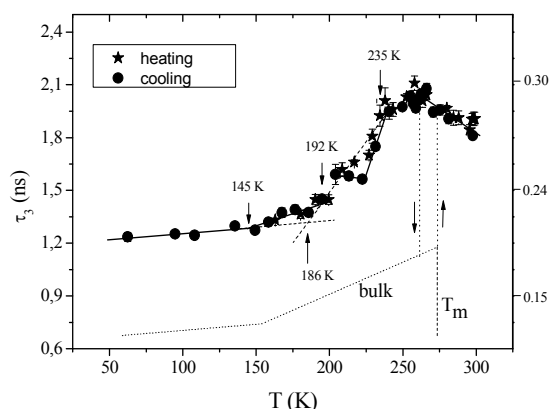

Figure 3. Dependence of relative intensity I_3 and I_4 on the coefficient of filling k.
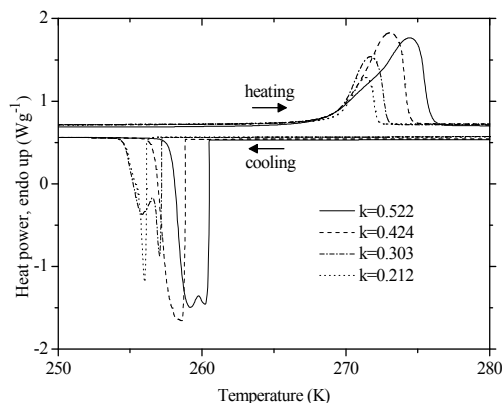

Figure 4. DSC curves exhibit a shift of solidification peaks towards lower temperatures with decreasing water content.

The glass transition temperature T_{gPALS} is determined as the intersection of lines for low temperature region and for heating regime in the region 200-240 K. This estimated value 186 K is in good agreement with the measurements on the water confined in matrices with smaller pore sizes [1]. The transformation area at T_{gPALS} is wide and more complex (mixture of glassy state and temperature dependence of τ_3 connected with creation of vacancies in crystalline ice, similar to bulk state [10]). Accordingly PALS measuremnts exhibit local changes of τ_3 (visible mainly in the cooling regime) and I_3 (see Fig. 6) at temperature below 231 K (solidification by homogeneous nucleation) as well as changes of I_3 in the temperature region of 230-273 K during different processes of freezing and melting in CPG pores.

Figure 5. Dependence of o-Ps lifetime τ_3 (or free-volume cavity size r_h) on the temperature T for confined ($k = 0.522$) and bulk water (dashed, from ref. [7]).
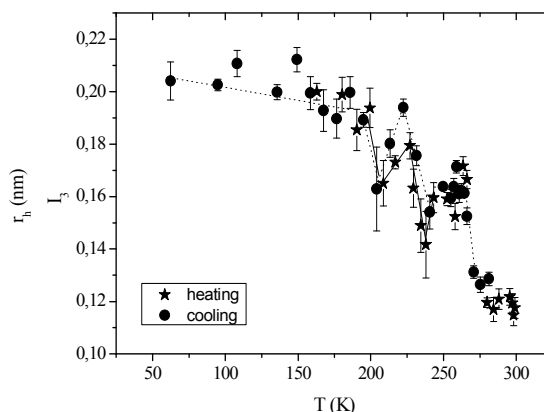
Figure 6. Dependence of relative intensity I_3 on the temperature T and $k = 0.522$.

Characteristic DSC curves exhibit hysteretic behaviour, i.e. crystallization in the pores is detected at lower temperatures compared to melting (Fig. 4), as observed in many previous studies [11].

Especially for the cooling regime dual thermal response is evident. While a scattering of onset of solidification peaks for individual measurement cycles of one sample usually reaches ~1 K, the difference between onset of freezing peaks for lowest and highest filling reaches at least 5 K. DSC thermogram shows a weak peak at 231 K in cooling cycle for all k. This peak is related to crystallization of confined water in the spherical cavities by homogenous nucleation [12,13].

The estimation of amorphous and crystallized fraction of water in CPG was based on the difference between the total enthalpy determined from DSC thermogram for cooling cycle relative to 1 g water and total enthalpy of pure water. Results are in Tab.1. From these results it follows that larger amorphous fraction is observed if water is absent in the central part of large pores of CPG.

Table 1. Content of water in the CPG samples expressed by coefficient k and estimated fraction of crystalline water from DSC measurements.

k	Crystalline fraction (wt%)
0.52	73
0.424	72
0.212	43

4. Conclusions

PALS temperature dependences confirm the presence of amorphous and crystalline phases of water confined in 12.6 nanometer pore size of CPG for the fully-filled pores. From the $\tau_3(T)$ dependence the glass transition temperature T_{gPALS} was estimated to the value 186 K. Confined water in CPG of the mesoporous category exhibits an evident dependence of thermal behaviour on the filling of the porous structure. This effect manifests itself by shift of DSC solidification peaks towards lower temperatures with decreasing water content. Proposed interpretation, based on the influence of microstructural properties on ice front percolation, is well supported also by the detected presence of solidification by homogeneous nucleation at typical temperature (231 K). The fraction of amorphous and crystallized water was estimated for different pore filling. The amorphous fraction is larger for the lower content of water in the CPG pores. Water escapes by evaporation from large pores with increasing of number of "empty" large pores (I_4 increase) with no significant changes of τ_4 (no thick layer on the inner pore surface) for $k > 0.1$.

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